



ADVANCES IN ORGANOMETALLIC CHEMISTRY

Volume 10

F. G. A. Stone &
Robert West

Advances in
ORGANOMETALLIC CHEMISTRY

VOLUME 10

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Advances in **ORGANOMETALLIC** ***CHEMISTRY***

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Contents

LIST OF CONTRIBUTORS	ix
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My Way in Organometallic Chemistry

A. N. NESMEYANOV

I. First Steps	1
II. The Diazonium Method	3
III. Homolysis and Heterolysis of Diazonium Salts. Synthesis of Halogenonium Salts. The Halogenonium Method	6
IV. Early Investigations into Organometallic Exchange Reactions.	9
V. Quasi-Complex Compounds	10
VI. Investigation of the Grignard Reaction	14
VII. Organometallic Tautomerism and Dual Reactivity	15
VIII. Fragmentation	22
IX. Stereochemistry of σ , σ - and σ , π -Conjugations	23
X. Stereochemistry of Electrophilic or Homolytic Substitutions	25
XI. Cyclic Compounds through β -Chlorovinyl Ketones	30
XII. Non-Transitional-Metal Vinyl Organometallic Compounds	34
XIII. Transition Metals and Metal Carbonyls	35
XIV. Ferrocene and Metallocenes	37
XV. Ligand Exchange in Ferrocene, Arene Cyclopentadienyl Derivatives of Iron	44
XVI. Cyclopentadienylmanganese Tricarbonyl and Cyclopentadienylrhenium Tricarbonyl	47
XVII. Organotitanium Compounds	50
XVIII. π -Allyl Complexes	52
XIX. σ -Arylated Complexes	55
XX. π -Acetylene Complexes of Transition Metals	56
XXI. Conclusion	59
References	60

Electronic Effects in Metallocenes and Certain Related Systems

D. W. SLOCUM and C. R. ERNST

I. Introduction	79
II. Homoannular Electronic Effects	80
III. Substituent Effects on the Ring-Metal Bond	91
IV. Substituent Effects on the Heteroatom, Oxidation-Reduction Potentials	98
V. Interannular Electronic Effects	101
VI. The Electronic Influence of Ferrocenyl and Related Groups as Substituents	107
VII. Conclusion	110
References	111

Nitrogen Groups in Metal Carbonyl and Related Complexes

M. KILNER

I.	Introduction	115
II.	Organonitrogen Derivatives	117
III.	Derivatives of Inorganic Nitrogen Groups	168
	References	186

Infrared Intensities of Metal Carbonyl Stretching Vibrations

S. F. A. KETTLE and I. PAUL

I.	Introduction	199
II.	Theory	201
III.	Measurement	204
IV.	Bonding	208
V.	Solvents	211
VI.	The Cotton-Kraihanzel Method	213
VII.	The Method of Local Oscillating Dipoles	214
VIII.	Bond Angles	216
IX.	CKM and Intensities	218
X.	Absolute Integrated Intensities	222
XI.	Conclusion	232
	References	233

Organometallic Aspects of Diboron Chemistry

T. D. COYLE and J. J. RITTER

I.	Introduction	237
II.	Some General Features of Diboron Chemistry	238
III.	Reactions of Diboron Tetrahalides with Unsaturated Compounds	251
IV.	Properties of Some Diboration Products	265
	References	269

Organo-Transition Metal Chemistry—A Guide to the Literature 1950-1970

M. I. BRUCE

A.	Textbooks	274
B.	Reviews.	281
C.	Primary Journals	285
D.	Abstracting Journals and Information Retrieval	288
E.	Conference Reports	290
F.	Synthesis	293
G.	Compound and Formula Registers	295
	References	296
	Appendix	297

Ligand Substitution in Transition Metal π -Complexes

A. Z. RUBEZHOV and S. P. GUBIN

I. Introduction	347
II. General Comments on Ligand Substitution in Complexes	348
III. π -Complexes with Ligands Stable in a Noncoordinated State	352
IV. π -Complexes with Ligands Unstable in a Noncoordinated State	371
V. Conclusion	409
References	409
AUTHOR INDEX	419
AUTHOR INDEX: REVIEWS OF ORGANO-TRANSITION METAL CHEMISTRY 1950-1970	445
SUBJECT INDEX	451
CUMULATIVE SUBJECT INDEX: VOLUMES 6-10	457
CUMULATIVE LIST OF CONTRIBUTORS	461
CUMULATIVE LIST OF TITLES	464

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My Way in Organometallic Chemistry*

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I. First Steps	1
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XIX. σ -Arylated Complexes	55
XX. π -Acetylene Complexes of Transition Metals	56
XXI. Conclusion	59
References	60

I

FIRST STEPS

Chemistry has charmed me since 1912 when I was thirteen, my passionate affections for various branches of biology (entomology, hydrobiology, ornithology) being already over. During my summer vacations at my grandmother's, I happened to come across an old shed of my grandfather's where I found the ancient treatise *Inorganic Chemistry* by Richter. This volume was more absorbing to me than the books of my favorite authors

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Jules Verne and H. G. Wells. A year later, I set up my own small laboratory and obtained Remsen's *Organic Chemistry*. This, and other books, strengthened my contact with elementary chemistry, so when in 1917 I crossed the threshold of Moscow University for the first time, I was quite familiar with the chemistry of those days. During my first years in the University I was enraptured by the science and nothing but the science of chemistry. As an undergraduate, however, as the challenges of inorganic, physical, and organic chemistry were overcome, I had to make a choice of specialization. I was fond of chemical substances, with their shape, color, and smell, whereas the generalizations of physical chemistry, however useful, seemed to me rather vague. But it was a difficult problem to choose between inorganic and organic chemistry, perhaps, that is why I took the essentially organometallic road. Not wishing to be Buridan's ass and die of hunger between two bundles of hay, I preferred to gather food from both bundles. Formally, however, I declared my adherence to the Organic Chemistry Division. This was caused by the fact that organic and analytical chemistry were headed by Professor N. D. Zelinsky, making this choice more attractive than any of the other possibilities. I was also much impressed by his proposal to work with him as a post-graduate student in 1922. By that time, the extensive scientific interests of Zelinsky were more and more concentrated on catalytic hydrocarbon chemistry, and his co-workers, whose number was constantly increasing, were exploring this field. Of course, this was very attractive and promising, but not for me. Carbon and hydrogen are good, but what about the other 100 elements? Though I was assigned a cyclopropane problem, I did not give it too much attention and looked for something closer to my own interests. Only after many failures, did Fortune in 1927-1928 show me her better face. I had been looking for esters of complex acids such as $\text{HHg}^{\text{II}}\text{I}_3$ or $\text{HPb}^{\text{II}}\text{I}_3$ and a possible isomerism of $\text{RPb}^{\text{II}}\text{I}_3$ with $\text{RPb}^{\text{IV}}\text{I}_3$. To begin with, the esters which had not been described should be synthesized. The direct reaction, e.g., CH_3I with HgI_2 , was obviously unsuitable. I attempted to obtain aromatics of the desired type by the decomposition of arene diazonium salts of the complex acids whose esters I was craving for. I prepared a series of such salts, among which were $(\text{C}_6\text{H}_5\text{N}_2)_4\text{Fe}(\text{CN})_6$ and $(\text{C}_6\text{H}_5\text{N}_2)_2\text{HgI}_3$. The decomposition of the former salt with or without Gatterman copper gave two compounds which were hard to separate and purify. One of them was lilac, the other colorless. Each had the composition $(\text{C}_6\text{H}_5)_2\text{H}_2\text{Fe}(\text{CN})_6$. I had no time to study them in more detail because simultaneously I had been

examining the decomposition of $(C_6H_5N_2)HgI_3$ and the results obtained were so interesting that they required my whole attention. So, my lilac and white compounds were never reported.

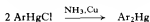
II

THE DIAZONIUM METHOD

The salt $(C_6H_5N_2)HgI_3$ decomposed completely within a few days. The resulting slurry could be purified to give a compound which, interestingly, had the composition $(C_6H_5)_2HgI_4$ (II), rather than that of the expected "ester" $C_6H_5HgI_3$ (I). I believed that the former compound was the ester of the acid " H_2HgI_4 " and introduced the compound into the reaction most typical of esters, alkaline saponification, viz. saponification by I^- . You can imagine my bewilderment when my ester reacted according to the scheme



Excess iodide made the mercuric iodide dissolve entirely, leaving a colorless dimeric "iodobenzene" which I had no difficulty in identifying as diphenyliodonium iodide. Thus, all my "esters" were diphenyliodonium salts whose anions were HgI_3^- or HgI_4^{2-} . This was a novel route to diphenyliodonium salts, but the disappointment was bitter. In this manner, the first publication containing concepts and experimental results which were my spiritual property appeared (I). However, the copper-initiated decomposition of the initial diazonium salts proceeded in quite another fashion. Instead of the yellow salts (I) and (II), I isolated high-melting plate-like crystals containing Hg, carbon, and iodine. But my glee did not last long. I was already sufficiently familiar with organometallic chemistry to suppose that the compound was nothing but C_6H_5HgI , which turned out to be precisely the case. One more disappointment. However, the reaction was an absolutely new way to organomercury compounds, so it was worth studying. "Double salts" such as $C_6H_5N_2^+HgBr^-$ or $C_6H_5N_2^+HgCl_3^-$, when treated with copper, produced C_6H_5HgBr or C_6H_5HgCl in good yields as well. Moreover, I showed that substituted arenediazonium salts, as well as each of the two naphthalenediazonium cations, afforded $ArHgCl$ compounds, while the "diazo method" as combined with the F. Hein symmetrization,



appeared to represent a one-step synthesis of diaryl mercury compounds. Based on this was my second publication (2), and also the third one (3), in collaboration with E. I. Kan (my first co-worker; she was by that time a student of the University). These have been followed by over 700 papers. The samples of $C_6H_5N_2HgBr_3$ and $C_6H_5N_2HgCl_3$ were left in unsealed ampoules. The second salt remained unchanged for years. The first one, in a year, gave a mixture of bromobenzene and a crystalline compound.

TABLE I
DIAZONIUM ORGANOMETALLIC SYNTHESIS^a

Metal	Reactions	% yield ^b	Reference
Hg	$ArN_2Cl \cdot HgCl_2 + 2Cu \rightarrow ArHgCl + N_2 + 2CuCl$ $2ArN_2Cl \cdot HgCl_2 + Cu + NH_3 \rightarrow Ar_2Hg + 2N_2$ $+ 2CuCl \cdot am + Hg$	30-80 30-80	(2) (3)*
Tl	$2ArN_2BF_4 + 2Tl \rightarrow Ar_2TlBF_4 + 2N_2 + 2TlBF_4$	approx 10	(5)
Sn	$ArN_2BF_4 + SnCl_2 + Zn \rightarrow Ar_2SnCl_2$ $+ (Ar_3SnCl + ArSnCl_3)$	10-40	(6, 7)
Pb	$4ArN_2BF_4 + PbNa \rightarrow Ar_4Pb + 4N_2 + 4NaBF_4$	15-30	(8)
Sb	$ArN_2Cl \cdot SbCl_3 + Zn \rightarrow ArSbCl_2 + N_2 + ZnCl_2$ $2ArN_2Cl \cdot SbCl_3 + 2Zn \rightarrow Ar_2SbCl_3 + N_2 + 2ZnCl_2$ $+ SbCl_3$	25-30 25-30	(9) (9)
	$3ArN_2Cl_3 \cdot SbCl_3 + 3Zn \rightarrow Ar_3Sb + 3N_2 + 3ZnCl_2$ $+ 2SbCl_3$	25-30	(9)
	$3ArN_2Cl \cdot SbCl_3 + 2Zn \rightarrow Ar_2SbCl_2 + 3N_2 + 2ZnCl_2$ $+ 2SbCl_3$	25-30	(9)
	$(ArN_2Cl)_2 \cdot SbCl_3 + 2Zn \rightarrow Ar_2SbCl + 2N_2 + 2ZnCl_2$	42-46	(10)
	$2ArN_2Cl \cdot SbCl_3 + Fe \rightarrow Ar_2SbCl_3 + 2N_2 + FeCl_2$ $+ SbCl_3$	42-97	(11)
	$ArN_2Cl \cdot SbCl_5 + 2CuCl \rightarrow ArSbCl_4 + N_2 + 2CuCl_2$	10-40	(12)
	$ArSbCl_2 + Ar'N_2Cl \cdot SbCl_3 \rightarrow ArAr'SbCl_3 + N_2 + SbCl_3$	—	(13, 14)
As	$2ArN_2Cl \cdot FeCl_3 + AsCl_3 + Fe \rightarrow ArAsCl_3 + N_2 + FeCl_3$ $+ FeCl_2$	20-40	(15, 32)
	$2ArN_2Cl \cdot FeCl_3 + AsCl_3 + 2Fe \rightarrow Ar_2AsCl + 2N_2$ $+ 2FeCl_3 + 2FeCl_2$	20-40	(16, 32)
	$3ArN_2Cl \cdot FeCl_3 + AsCl_3 + 2Fe \rightarrow Ar_3As + 3N_2$ $+ 3FeCl + 3FeCl_2$	—	(15, 32)
	$ArAsX_2 + (Ar'N_2Cl)_2ZnCl_2 + 2Fe \rightarrow ArAr'_3As + 2N_2$ $+ ZnCl_2 + 2FeCl_2$	30-40	(16, 32)
Bi	$3ArN_2BF_4 + 2Bi \rightarrow Ar_3Bi + 3N_2 + Bi(BF_4)_3$	20-70	(17, 18)

^a All reactions are carried out in acetone or (in the case of Sb) in ethyl acetate; am is ammonia.

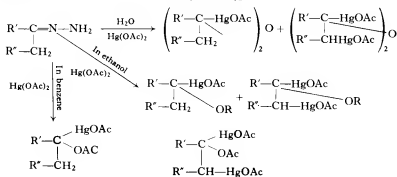
^b The yield range refers to various aryls, Ar. The yields are the highest with C_6H_5 .

If I had worked up the mixture (as I subsequently did in 1959), diphenylbromonium (and diphenylchloronium) salts could have been reported some thirty years before their actual discovery (4).

But the "diaz method" still had its grip on me. Which metals, apart from mercury, could be subjected to the method? To answer this, many years were to pass because simultaneously I was working on other problems of interest to me. Eventually, the method of synthesis was extensively developed for aromatic derivatives of such elements as Hg, Tl, (Ge), Sn, (Pb), As, Sb, Bi. For the metals in parentheses the method was shown to just work, while for the others it is an excellent preparative procedure. In Table I the best versions are exemplified. At the same time, I and the first generation of my disciples, and also other scientists, applied the method to various organomercurials substituted at the aromatic nucleus (19-21), and to the naphthalene (22), triphenylmethane (23), and pyridine (24) series.

This work was initiated in 1927, and in 1953 the last paper of the series was published. Intermittently, other related investigations were accomplished. Here, I would like to mention the reaction of aliphatic diazo compounds with mercuric chloride. The reaction of methylamine with mercuric chloride under the conditions of the diazo method was unsuccessful. Instead of the methylmercuric chloride expected, the synthesis gave negligible amounts of chloromethylmercury chloride, a compound obtained by Hellerman from mercuric dichloride and diazomethane in good yield. With diazoacetic ester, the compound $\{ClHg(Cl)C(=O)OC_2H_5\}_2Hg$

was obtained (25). Finally, hydrazones of ketones which might form the aliphatic diazo intermediates gave a number of organomercurials in a reaction which, as it was suggested, involved conjugate addition [Nesmeyanov, Reutov, and Loseva (26, 26a)].



The conjugate addition of HgOAc and the solvent fragments (RO in methanol, $-\text{O}-$ in water, OAc in benzene) was usually accompanied by the mercuration of the methylene adjacent to the unsaturated carbon atom. In addition, elimination of the second mercury-containing group attached to the β -carbon, together with the solvent fragment attached to the α -carbon sometimes occurred, giving an α,β -double bond. For example, cyclohexanone produced 1-acetatomercurycyclohexene-1. This β -elimination correlated with the properties of quasi-complex compounds which had been investigated by us extensively.

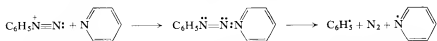
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HOMOLYSIS AND HETEROLYSIS OF DIAZONIUM SALTS. SYNTHESIS OF HALOGENONIUM SALTS. THE HALOGENONIUM METHOD

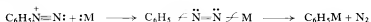
The aliphatic diazonium salts were only a side issue in the research. At the same time, the aromatic tetrafluoroborate salts were studied by me from other points of view. These investigations are outside the framework of organometallic chemistry but they must be described here briefly, otherwise the logical sequence would be lost. Waters (27), Hey (28), and other investigators who were concerned with free-radical chemistry had shown that diazo compounds produce organometallic compounds via free radicals. Sandin, McClure, and Irwin (29) found a similar reaction, and proposed a similar mechanism for formation of diaryliodonium salts. The analogy enabled me and Makarova to draw the iodonium and diazonium investigations together. We were interested in whether conditions existed which would make both onium types decompose heterolytically, rather than homolytically. The tetrafluoroborates, in particular, seemed unable to display homolytic decomposition. This is because the reaction would lead to atomic fluorine. Indeed, diphenyliodonium tetrafluoroborate proved to be an excellent heterolytic arylating agent.

Thus PPh_3 , AsPh_3 , SbPh_3 , SPh_2 , SePh_2 , and a number of nitrogen-containing bases, when fused with Ph_2IBF_4 , were phenylated, giving onium compounds in very good yields (30, 31). The phenylation of pyridine was especially effective; diphenyliodonium tetrafluoroborate arylated it (heterolytically) at the nitrogen exclusively to yield phenylpyridinium salts, while the corresponding chloride reacted homolytically and gave nothing but a mixture of pyridines C-phenylated at the nucleus (32).

Similarly, benzenediazonium tetrafluoroborate arylated pyridine, but homolytically, and produced a mixture containing α - and β - rather than *N*-substituted compounds. Heterolytic arylation occurs with nitrobenzene or a phenyltrimethylammonium salt (30), giving the meta isomers, whereas the Gomberg arylation reaction gives a mixture in which the para isomer prevails. We explained this by assuming that the benzenediazonium cation might give the diazo species with pyridine or other Lewis bases, so that the reaction would be directed along the homolytic path.

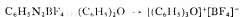
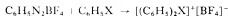


Like other diazonium salts, the tetrafluoroborates decomposed when treated with metal powders, and this process may resemble the above reaction.



This also explained the role of tetrafluoroborates and other complex anion salts in the organometallic syntheses described above.

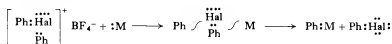
The most impressive result was the synthesis of diphenylbromonium tetrafluoroborate (30, 33, 34), diphenylchloronium tetrafluoroborate (30, 35), and triphenyloxonium tetrafluoroborate (30, 36) by decomposing benzenediazonium tetrafluoroborate in bromobenzene, chlorobenzene, and diphenyl ether, respectively (Nesmeyanov, Tolstaya, and Isaeva).



Spontaneous decomposition of $\text{C}_6\text{H}_5\text{N}_2\text{HgBr}_3$ was also a source of diphenylbromonium salts (4). Diphenylbromonium and, especially, triphenyloxonium salts proved surprisingly stable towards electrophiles, and could be nitrated under drastic conditions to give the meta-substituted halogenonium and para-substituted oxonium cations (37). On the other hand, they arylated nucleophiles readily (38).

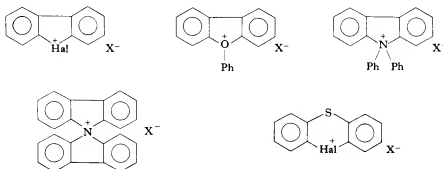
The halogenonium series $\text{Ar}_2\text{Hal(X)}$ and $\text{ArAr}'\text{Hal(X)}$ were synthesized and studied. They resembled iodonium salts very closely; for example, the respective iodides, when treated with Hg or Sn (but not Tl, Pb, Bi) powders, produced the organometallics in a yield up to 60% (39), in analogy with the reaction reported by Sandin, McClure, and Irwin (29) for diphenyliodonium salts.

Diphenylbromonium tetrafluoroborate gave 15% to 20% of the expected organometallics with Tl, Sn, Pb, Bi (but not Hg) powders (40). Perhaps, the better reactivity of the tetrafluoroborate as compared with the iodide may be explained in the same manner as with the diazonium arylation. This may be written as follows:



Noble metals such as Ag, Hg, and Pt do not react in this manner. Neither the iodide nor the tetrafluoroborate of the triphenyloxonium cation react with any of the metal powders, apparently because oxygen cannot expand its octet.

Thus, the diazonium synthesis of organometallic compounds had been extended to the onium synthesis, whatever its versatility and limitations. The analogy had to be completed and further extended. This was performed by my disciple O. A. Reutov and his co-workers (41), who showed that the salts $\text{Ar}_2\text{IHgCl}_3$, $(\text{Ar}_2\text{I})_2\text{SnCl}_6$, $\text{Ar}_2\text{ISbCl}_4$, and $(\text{Ar}_2\text{I})_2\text{BiCl}_3$ gave satisfactory yields of the appropriate organometallics on reaction with metal powders (Reutov, Ptitsyna). Similar syntheses were achieved with diphenylbromonium and -chloronium salts, which yielded the derivatives of Hg, Tl, Sb, Sn, and Bi (40). Of course, the halogenonium method, unlike diazonium synthesis, can hardly be of preparative value, but this does not reduce its cognitive importance. Also, in collaboration with Tolstaya, Grib, and others, we studied the chemistry of onium compounds *per se*, and applied the heterolytic decomposition mentioned above to the synthesis of a number of heterocycles as shown in the accompanying scheme (42).



This short survey of our investigations on onium compounds is incomplete if we do not mention a novel synthesis of diaryliodonium salts discovered in collaboration with Freidlina (43);



and also work concerning Wittig "ate" complexes (44), performed in collaboration with Sazonova. We found possibly the simplest way to synthesize salts of the anion BAR_4^-



and obtained compounds where Ar is not only aryl but heterocyclic as well.

IV

EARLY INVESTIGATIONS INTO ORGANOMETALLIC EXCHANGE REACTIONS

Now, I must refer to the early 1930s when the diazo method had allowed me to prepare various compounds of the type Ar_2Hg and ArHgCl . It seemed desirable to use these compounds for the synthesis of other organometallics. Together with my colleague K. A. Kocheshkov (45, 46), who had started his well-known organometallic research by studying organotin compounds, we discovered the reaction



which proved to be a good way of obtaining organotin aromatics. In ethanol, if the Kharasch electronegativity of the radical R was sufficient, a side reaction occurred and an organometallic was not obtained.



In acetone the situation was somewhat better, but possibly because the acetone-enol was involved, the side reaction still sometimes predominated. In ligroin, however, though SnCl_2 is hardly soluble in this solvent, all complications were avoided (47) and a number of organotin aromatics were synthesized and studied (46). Later the reaction was applied to the synthesis of chlorovinyl derivatives of tin (48). Organotin compounds of the type $(\text{C}_2\text{H}_5)_2\text{Sn}$ or $[(\text{C}_2\text{H}_5)_3\text{Sn}]_2$ were also able to abstract aromatic groups from mercury and thus give $\text{Ar}_2\text{Sn}(\text{C}_2\text{H}_5)_2$ or $\text{ArSn}(\text{C}_2\text{H}_5)_3$, while the

reaction was the first source of organotin phenol or dimethylaniline derivatives (49). The compounds R_2TlX reacted with $SnCl_2$ in an analogous manner and produced R_2SnCl_2 and $TlCl$ (50).

The organomercurials R_2Hg could also be used to obtain the organo derivatives of zinc (51), cadmium (52), and aluminum (53) *via* the exchange process



Inter alia, aromatic ring-substituted compounds Ar_2Zn , Ar_2Cd , and Ar_3Al were prepared and their properties studied.

Another branch of the work was concerned with a reverse reaction, the interaction of mercury dichloride with organometallic compounds of Groups III, IV, or V. At that time, (1934), the literature on the reaction was surprisingly scarce.

It was found that mercury dichloride in neutral media readily abstracted phenyl groups from Ar_4Sn , Ar_3SnCl , Ar_2SnCl_2 , $ArSnCl_3$, Ar_4Pb , Ar_3PbCl (but not Ar_2PbCl_2), $ArSbCl_2$, or Ar_2SbCl , and formed the $ArHgCl$.

In alkaline media all the above compounds, except for Ar_4Pb or Ar_2PbCl_2 , formed Ar_2Hg almost instantaneously when treated with mercury dichloride (or mercuric oxide) (54). The compound $ArB(OH)_2$ behaved similarly. $RHgOH$ could be arylated in alkaline media in the same fashion; thus a new synthesis of unsymmetric $RHgAr$ compounds was ready for use (Freidlina, Kocheshkov, Nesmeyanov) (55).

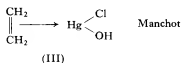
The arylation reactions described in this section were used not only synthetically but also for analysis of structures of "quasi-complex" compounds of mercury.

V

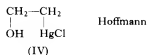
QUASI-COMPLEX COMPOUNDS

Whoever is concerned with the organometallic chemistry of mercury cannot help admiring the striking compounds formed from olefins or acetylenes and mercuric salts, and the classical papers by K. Hoffmann, Schöller, Schraut, Kuchero, and their successors. Although the controversy as to the structures of the adducts, which had been discovered in 1920–1925, was not so sharp as before because increasingly evidence was accumulated in favor of a formulation with a mercury-carbon σ -bond, no one could forget the work of W. Manchot (56), who had been trying to show that the adducts might be, in modern notation, π -complexes. The

fact that acids or other reagents could produce Hg^{2+} and make the adducts lose olefin, made the adducts seem analogous to Zeise's salt, and raised the questions as to whether, for example, Hoffmann's ethanolmercurichloride should be formulated as

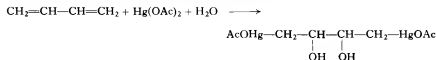


or as



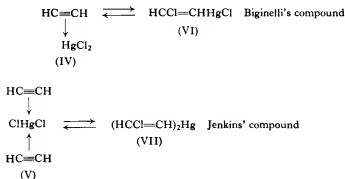
The first structure, if arylated by $\text{C}_6\text{H}_5\text{SnOOH}$ in alkaline medium according to the procedure developed by us [see above (55)], should lead to diphenylmercury and ethylene, while the second structure should give the unsymmetrical organomercurial $\text{HOCH}_2\text{CH}_2\text{HgC}_6\text{H}_5$.

In reality, the second possibility occurred (57), and the same was true for the adducts containing other olefins. Finally, we verified the presence of hydroxyl in structure (IV) through reaction with phenyl isocyanate. Thus, the convincing experiments of Hoffmann, Middleton, and R. Adams were confirmed by our decisive evidence, so that π -structures were condemned to fade from the scene for these compounds. However, to emphasize the behavioristic similarity with the π -complexes, I suggested the term "quasi-complex" for the compounds which are formed from metallic salts and olefins or acetylenes through addition to the π -bond. A number of such quasi-complex compounds were obtained and studied by us. In particular, we showed that butadiene or its homologs, contrary to the earlier opinion of Sand, also formed the quasi-complex adducts in water, e.g.,



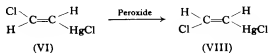
Other adducts were also prepared, namely, those of allylcyclopentane, 2-allyldecalin, diallyl ether, and diallylamine. The latter three compounds are oxygen or nitrogen-heterocycles. They all are quasi-complexes [Nesmayanov, Lutsenko (58, 59)].

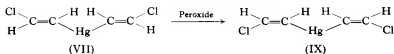
With the adducts from mercury dichloride and acetylene, we [Nesmeyanov, Freidlina, Borisov (60-62)] began the investigation by studying the compounds of Biginelli and Jenkins for which either π or σ -structures, or tautomerism between these might be assumed.



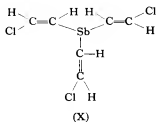
Here, the action of I^- , CN^- , $\text{S}_2\text{O}_3^{2-}$, or even of such a complexing agent as PPh_3 , led to the elimination of the mercury salt and the quantitative formation of acetylene. In addition, our method of phenylation with PhSnOOH produced diphenylmercury and acetylene.

This seemed to establish the π -complex nature of the compounds. Other reactions, however, suggested the organometallic chlorovinyl structures, e.g., the reaction with iodine leading to iodochloroethylene, or the transfer of chlorovinyl from one metal to another, described more extensively below. This raised a question: Were, perhaps, the complex and the chlorovinyl species tautomers of a new kind, i.e., could there be an equilibrium isomerism of the type $(\text{IV}) \rightleftharpoons (\text{VI})$ and $(\text{V}) \rightleftharpoons (\text{VII})$? Our final answer was, No. In other words, the chlorovinyl structures (VI) and (VII) were correct and tautomerism was absent. Actually, we found that (VI), (VII), (VIII), and (IX) existed as geometric isomers, the isomers (VI) and (VII) having a trans configuration while (VIII) and (IX) had a cis configuration. The compounds strictly retain their configurations when dissolved in various solvents in the absence of light or peroxides, so that tautomerism is ruled out.





The *cis* isomers are more stable than the *trans* isomers, so they may be prepared from the *trans* compounds by treating with peroxides or on irradiation (63, 64). Moreover, *cis*-chlorovinylmercury chloride could be obtained from acetylene and mercury dichloride vapors [Freidlina, Nogina (65)] and symmetrized by ammonia to give (IX), which retained the initial configuration (66). Finally, *cis*-chlorovinylmercury chloride could be synthesized from mercury dichloride and acetylene.



This reaction produced a mixture of (VI) and (VIII) from which pure (VIII) was isolated (67).

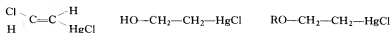
The compounds (VIII) and (IX) display their quasi-complex properties less clearly than do (VI) and (VII). Their *trans* isomers lose acetylene much more easily than do the *cis* ones.

We [together with Borisov (68)] prepared chlorovinyl compounds of antimony by saturating SbCl_5 with acetylene, distilling off $(\text{ClCH}=\text{CH})_3\text{SbCl}_2$, and reducing the distillate to $(\text{ClCH}=\text{CH})_3\text{Sb}$ (X). This procedure afforded pure *trans*-($\text{ClCH}=\text{CH})_3\text{SbCl}_2$ as well as the *cis-trans* species (X) [from $(\text{ClCH}=\text{CH})_3\text{SbCl}_2$], which was initially thought to be a pure *cis* form. All these compounds are also of the quasi-complex type.

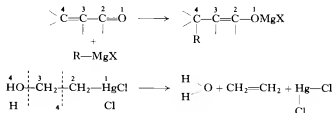
In other studies, with N. K. Kochetkov (69, 70), we obtained the compounds $\text{R}(\text{Cl})\text{C}=\text{C}(\text{HgCl})\text{R}'$ from the appropriate acetylenes. Quasi-complex elimination of the $\text{RC}\equiv\text{CR}'$ was especially easy, just by treating with sodium chloride in cold water, when R or R' were carboxyl groups.

Why do quasi-complex compounds liberate acetylene or olefin so

readily? The answer was as follows [Nesmeyanov, Freidlina, Borisov (60, 71)]. The polarizability of Hg—C bonds shows its effect in these compounds:



The positions of the Cl—C, HO—C, and RO—C bonds allows them to conjugate with the Hg—C bond ("σ,σ-conjugation"). Hence, an electrophile (with the latter two substrates), or an agent which can bind Hg²⁺, or a reagent which combines both properties, such as HCl, will break the conjugated σ-bonds, create at the center of the molecule the new π-bond, and eliminate olefin or acetylene. This is formally similar to the 1,4-addition occurring in π,π-conjugated systems.



The 1,2 and 3,4 bonds are broken, the atoms 1 and 4 add fragments of a reagent, and the new π-bond, positioned between carbon atoms 2 and 3, appears. However, a π,π-conjugated molecule does not lose its integrity, whereas the σ,σ-conjugated system undergoes the rupture of its 1,2 and 3,4 σ-bonds, with elimination of the central fragment. The analogy would be more than simply formal if both reactions involved a cyclic transition state, but this was never verified. Thus, we established the concept of the "quasi-complex" compound, characterized by a pronounced σ,σ-conjugation. This led to a better understanding of the peculiar reactivity of σ,π-conjugated systems as well (71, 72).

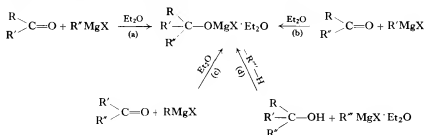
VI

INVESTIGATION OF THE GRIGNARD REACTION

This research commenced with the same motive as that discussed in the preceding section. Namely, were the products arising from the Grignard alkylation of oxo compounds π-complexes or, as suggested by Grignard,

were they alkoxides formed through addition of the R and the MgX moieties to the C and O of the carbonyl group, the π -bond having been broken. This work, performed in collaboration with V. A. Sazonova and other co-workers, was stimulated by the papers of Hess (73), and Rheinboldt and Roleff (74), who published their evidence in favor of the complex nature of the adducts in 1921–1924.

We showed that the four routes outlined below all led to one and the same crystalline compound, while route (d) proved the alkoxide structure of the magnesium derivative unambiguously (75). Hence the hypothesis of Grignard, not that of the German workers, is correct.



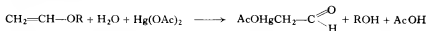
Also, experimental problems not considered by the adherents of the complex theory were observed (76). For example, it was found that the precipitate formed from fenchone and $\text{C}_6\text{H}_5\text{MgBr}$ in ether and earlier claimed to be the Grignard reagent/ketone complex (the ketone indeed could be regenerated from the complex) contained MgBr_2 rather than $\text{C}_6\text{H}_5\text{MgBr}$.

VII

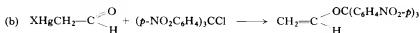
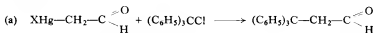
ORGANOMETALLIC TAUTOMERISM AND DUAL REACTIVITY

We (Nesmeyanov, Freidlina, Borisov) had discovered dual reactivity when studying the behavior of the adducts formed from mercury salts and unsaturated compounds, especially acetylene. The adducts reacted both as complexes and as chlorovinyl metal compounds. As previously mentioned, dual reactivity was explained by σ, σ -conjugation. Later we [Nesmeyanov, Lutsenko (77, 78), Perevalova (79)] found that the σ, π -conjugation was of no less significance. Vinylic ethers or esters treated with mercury

acetate produced aldehydes and ketones with HgOAc groups in the α -position (78, 80).

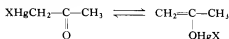


Similarly, R_3SnOCH_3 and $\text{CH}_2=\text{C}(\text{CH}_3)\text{OCOCH}_3$ gave the α -stannylated ketones $\text{R}_3\text{SnCH}_2\text{COCH}_3$ (81). All these oxo compounds possessed an extremely reactive metal atom and could be alkylated or acylated at either the carbon or the oxygen atom, depending on the reactant. I termed this phenomenon reaction site transfer. Actually, the reaction site embraced the conjugated (σ, π -conjugated in the reactions mentioned) system, for instance

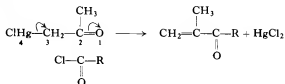


Similar reactions occur with α -chloromercury ketones. Reactions of type (a) are less representative than those of type (b): acyl chlorides, aryl sulfonyl chlorides, and dialkylchlorophosphites react according to type (b) and display reaction site transfer. Is this a result of keto-enol tautomerism ("mercuotropy")? Can metallotropic tautomerism occur? Or, alternatively, can the ambivalent behavior be explained by "reaction site transfer," which in this case involves the σ, π -conjugated system?

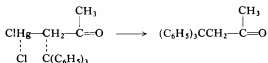
We ruled out tautomerism, viz.,



Thus α -C-organometallic derivatives of oxo compounds are, as a rule, acylated or alkylated at the oxygen atom, the reaction site being transferred as in the scheme

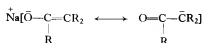


Again, as with all conjugated systems, as well as the quasi-complex compounds, the 1,4-attack takes place so that the 3,4 σ - and the 1,2 π -bonds are broken, while the 2,3 π -bond is formed. The process very probably involves a six-membered transition state. A four-membered state may participate in C-alkylation where the reaction site is not transferred.



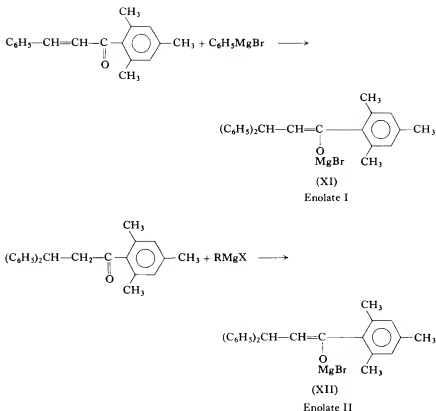
This, and many other results (80–88), led us to the problem of the dual reactivity of metal enolates. We prepared (89) the simplest enolates such as $\text{CH}_2=\text{CHOLi}$ and $\text{CH}_2=\text{CHONa}$ by reacting the mercury derivative of acetaldehyde with the respective metal.

Dual reactivity of metal enolates had been known for years, e.g., for the sodium derivative of acetoacetic ester. It was rationalized in two essentially different ways: (1) first, the enolates were thought to be tautomeric [Hückel (90)]; (2) later they were supposed [Arndt, Eistert (91)] to be ionic and to exist as mesomeric ions

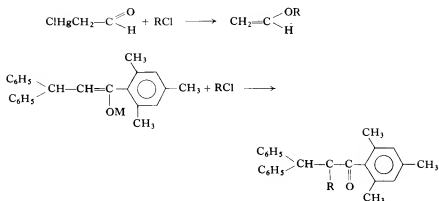


with two reactions sites, thus being able to display dual reactivity. We approached the problem stereochemically, based on the results obtained with the acetylene quasi-complexes. Together with Sazonova (92), we considered the results of Kohler, Tishler, and Potter (93), who prepared two stereoisomeric BrMg enolates of diphenylpropionemesitylene. One of the enolates was obtained through the 1,4-addition of $\text{C}_6\text{H}_5\text{MgBr}$ to benzoyl-acetomesitylene, the other from diphenylpropionemesitylene enolized by a Grignard reagent.

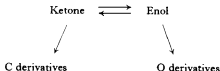
We found that the stereoisomeric lithium (94) or sodium (95) enolates showed precisely the same stereoisomerism. Benzoylation of the enolates (XI) and (XII) gave the appropriate stereoisomeric benzoates. Hence, the enolates are not subject to steric isomerization under these conditions. Consequently, no C-metallic derivative of the ketone species is involved, otherwise it would function as an intermediate, allowing the stereoisomeric enolates to isomerize to an equilibrated mixture. Indeed, if a tetramethylammonium salt whose cation cannot form any covalent bond with oxygen is



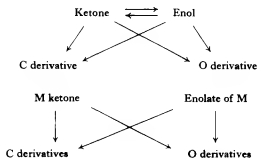
added to either (XI) or (XII), then the enolates do isomerize to give the same benzoate mixture, whichever enolate, (XI) or (XII), is benzoated. Thus, the enolate structures of the BrMg, Li, and Na-derivatives were proved, as well as the fact that neither the C—M ketone tautomer nor any ion (hence no mesomeric ion) are present in the benzene solution. However, the enolates may be both *O*- and *C*-alkylated. For example, each of them, when treated with $\text{CH}_3\text{OCH}_2\text{Cl}$, produced the same mixture of the CH_3OCH_2 - α -substituted ketone and the CH_3OCH_2 -ether of the enol. We separated the mixture and showed that the ethers had the *cis* or *trans* configuration, depending on that of the initial enolate. Therefore, the reaction site is transferred over the $\sigma\text{-O}-\text{C}=\text{C}=\text{C}-\pi$ conjugated system. Note the curious antiparallelism between this reaction and the alkylation of the mercury derivative of acetaldehyde:



In this manner, both *C*- and *O*-metallo derivatives of keto-enol systems were shown not to be in tautomeric ketone \rightleftharpoons enolate equilibrium (in benzene), thus differing from ketones and enols themselves where ketone \rightleftharpoons enol equilibria exist. Metal enolates, however, are transformed by substitution to the derivatives of the ketone species, while our *C*-mercury derivatives of ketones or aldehydes have been shown to produce the enol compounds. A conventional scheme (in which ketones, not their metallic derivatives, are shown) thus becomes somewhat unsatisfactory:



It may be replaced by another which assumes that a tautomeric equilibrium does not govern the dual reactivity, but may or may not accompany the process.



The *C*-substituted derivative may be synthesized directly from the enol (or enolate) while the *O*-substituted derivative may be prepared from the ketone, through reactions in which the reaction site is transferred over the conjugated system. In other words, this occurs due to the T-effect (inducto-meric effect in the case of the σ,σ -conjugated systems). This invalidates the Knorr pseudomery, which we believe should be eliminated from scientific usage [see the survey paper written by M. I. Kabachnik and myself and presented by me to the IUPAC Congress in Zürich, 1954 (96)]. The above concept applies not only to keto-enol systems and their metallic derivatives, but also to the entire concept of dual reactivity. The lecture mentioned above and the paper of reference (72), systematized the tautomerism and conjugation phenomena. We suggested the classification of the conjugation phenomena which govern both reaction site transfer and dual reactivity given in Table II. Today, the terms π,π -; σ,π ; σ,σ ; and p,π -conjugation are so extensively employed in the literature that no reference is given.

TABLE II
CONJUGATION PHENOMENA

Symbol	Structural notation	Typical system	Typical reaction
π,π		$\text{CH}_2=\text{CH}-\underset{\text{R}}{\text{C}}=\text{O}$	$\xrightarrow{\text{R'MgBr}} \text{R'CH}_2-\text{CH}=\underset{\text{R}}{\text{C}}-\text{OMgBr}$
σ,π		$\text{ClHg}-\underset{\text{R}}{\text{CH}_2}-\text{C}=\text{O}$	$\xrightarrow{\text{HCl}} \text{Cl}_2\text{Hg} + \text{CH}_2=\underset{\text{R}}{\text{C}}-\text{OH} \rightleftharpoons \text{CH}_3-\underset{\text{R}}{\text{C}}=\text{O}$
σ,σ		$\text{ClHg}-\text{CH}=\text{CH}-\text{Cl}$	$\xrightarrow{\text{I}^-} \text{HgI}_2 + \text{HC}=\text{CH} + 2\text{Cl}^-$
p,π		$\text{RO}-\underset{\text{R}}{\text{CH}}=\text{CH}_2$	$\xrightarrow{\text{H}_2\text{O}^+} \text{ROH} + \text{O}=\text{CH}-\text{CH}_3$
p,p		$\text{R}-\underset{\text{OR}}{\overset{\text{OR}}{\text{P}}}=\text{O}$	$\xrightarrow{\text{CH}_3\text{I}} \underset{\text{OR}}{\overset{\text{OR}}{\text{P}}}=\text{O}-\text{CH}_3 + \text{RI}$

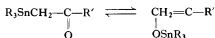
The examples in Table II serve to clarify the classification; discussing it in more detail would take too much space. This research was a starting point

for M. I. Kabachnik, who investigated tautomerism as an equilibrium-reversible isomerization. By using the Brönsted-Izmailov theory of acid-base equilibrium he constructed the quantitative theory of tautomeric equilibrium. But this topic would lead us too far from our story.

After Lutsenko, Sazonova, and Nesmeyanov had established that there are metallic derivatives of tautomeric systems which are neither mesomers nor tautomers, we (together with Kravtsov) attempted spectroscopic studies of organometallic derivatives akin to a number of tautomeric or virtually tautomeric systems. For this purpose we selected metals whose bonds with cation-accepting centers of a tautomeric system were of low polarity. As a rule, the spectra showed only one structure of the organometallic derivative to be present (97-101) which either did or did not coincide with the structure of the initial compound (100, 101). With organometallic derivatives of nitroso phenols (102-104) or of sulfonyl aminopyridines (103, 105), the equilibrium of the two tautomers was determined, its position depending on the solvent, on substituents attached to the tautomeric system, and on intramolecular coordination. Thus, metallotropic tautomerism, a rather exotic phenomenon, was discovered. In crystals of the organometallic derivatives discussed here there may exist intermolecular mesomerism caused by coordination of an organometallic group with the second cation-accepting center of the tautomeric system (106, 107). Spectral parameters obtained in a study of the structures depend on the electron density distribution; therefore the problem arises as to how electronic effects of the organometallic groups depend on the solvent and on the intra- or intermolecular coordination. It was found that the electronic effects vary significantly, influenced by specific solvation (108) or by coordination (108, 109). The intermolecular coordination in the crystal obscures the intramolecular electronic effects in the molecules of organometallic derivatives of non-transitional metals (109, 110). Organomercury groups are more apt to coordinate intramolecularly than similar organotin or -lead substituents (108, 111), while organotin groups are more efficient at coordinating inter- than intra-molecularly (107).

Our investigations carried out in collaboration with Lutsenko (83, 87), and subsequently the research by Lutsenko, Baukov, and others, were aimed at the study of rearrangements and tautomerism of organometallic derivatives of keto-enol systems (112-114). This work showed that α -silylated compounds of the type $R_3SiCH_2C(O)CH_3$ might irreversibly rearrange into $CH_2=C(OSiR_3)CH_3$, although they are not tautomeric.

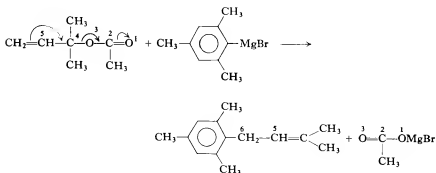
α -Organotin derivatives of aldehydes or ketones synthesized from the alkoxides R_3SnOCH_3 and vinyl ethers were shown to be tautomeric



equilibrium being reached much faster in the presence of a triorganotin halide catalyst. The allelotropic mixtures obtained from ketones containing various R' groups contained 6% to 25% of the O isomer and the value was as high as 80% for the aldehyde ($R = C_3H_7$). A similar tautomerism, accomplished by slow equilibrium reactions, was found by Lutsenko *et al.* for α -trialkylgermyl ketones as well. Thus, in addition to metallotropic tautomerism, which was shown by Kravtsov and the author to involve similar atoms (two oxygens or two nitrogens), heteroatomic C—O metallotropy was also discovered.

VIII FRAGMENTATION

We hope to have demonstrated that a σ, σ -conjugated system, if attacked at its extreme points, will undergo β -elimination, e.g., the quasi-complex adducts will eliminate acetylene or olefin. Longer systems which include different alternations of σ - and π -conjugated systems are also possible. If a σ -bond is centered in a conjugated chain, an attack directed at, for example, the 1,6-position, will break the molecule. Such a reaction searched for and found by us (together with Freidlina and A. Kochetkov) is shown below (115, 116).



We studied a number of similar reactions (116, 117). Later analogous reactions were reported (118) and termed fragmentations. Apparently, the β -elimination is a fragmentation and one of the most widespread ones at that. Both phenomena are caused by the σ,π - or σ,σ -conjugations.

IX

STEREOCHEMISTRY OF σ,σ - AND σ,π -CONJUGATIONS

I was interested in the stereochemical behavior of conjugated σ -bonds. I considered the β -eliminations reported earlier as well as those found by us with the chlorovinyl compounds, and came to the conclusion (119) (which did not seem so trivial in 1950) that the eliminations require that the eliminating groups be trans-oriented. Hence, σ,σ -conjugation will be more complete if the bonds are parallel. In the late 1940s it was a good assumption to check, so we [together with I. I. Kritzkaya (120)] carried out the following experiment.

The Razuvaev organomercuric synthesis gave us σ -chloromercuri-camphenilone via camphenonoyl peroxide.



The mercury-carbon bond of this bicyclic ketone is fastened almost perpendicularly to the plane of the carbonyl π -orbital. This perpendicularity may be solely responsible for the fact that the compound, unlike the α -mercured open-chain oxo compounds, possesses a quite inactive mercury atom. While the compounds $\text{ClHgCH}_2\text{C(O)R}$ are instantaneously hydrolyzed or alcoholized in the presence of I^- , and readily react with triphenylchloromethane or with acyl chlorides, α -chloromercuricamphenilone reacted neither with these agents nor even when refluxed with concentrated hydrochloric acid for a long time. Together with Kursanov, Pecherskaya, and Parnes (121) we studied deuterium exchange in camphenilone and camphorquinone



as compared with 2,2,2,6-trimethylcyclohexanone, and found that the latter compound exchanged its hydrogen for deuterium noticeably while the former two, wherein the σ -bond axis is perpendicular to the π -bond plane, not at all. Ketones of the camphenilone type could not be nitrosated or sulfonated either (122). This inactivity of the α -hydrogen of the camphenilone may be explained in the same manner as with the mercurated compound. Moreover, the Bredt rule may be applied in this case because the double bond in the enol would appear at the bridgehead carbon. This no longer holds for the mercury derivative. Another explanation, which would account for the inactivity of halogen attached to a bridgehead atom stems from the impossibility of the Walden inversion, but this is also invalid in our case because the reaction is of the S_N2 type, hence configuration is retained (see below). Thus we necessarily came to the conclusion which is today almost obvious, that there is zero overlap of the σ - and π -orbitals when the axis of the former orbital is perpendicular to the plane of the latter. In 1956, Corey and Sreen (123), who were apparently unaware of my lecture and paper (reported in 1950), published a similar concept exemplified by enolization of cyclic ketones whose α -C—H bonds were axial or equatorial.

Together with Tolstaya, we tried to synthesize quinuclidone in 1949–1950. We thought that the analogous geometry of the nitrogen lone pair and the carbonyl π -orbital would destroy amide conjugation, hence the compound would be as basic as an amine usually is. This proved to be correct. Quinuclidone, synthesized by Rubtsov (124), is a base at least as strong as amines and far stronger than amides, while its CO



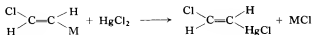
behaves as a ketonic group [see also (124a)].

Another example of geometrical hindrance acting on the σ, π -conjugation is the chelated metal acetylacetonates. We [together with Kursanov, Smolina, and Parnes (125)] showed that, unlike acetylacetone, cobalt (III) or aluminum acetylacetonates did not exchange their protons for deuterium with D_2O in dioxane.

X

STEREOCHEMISTRY OF ELECTROPHILIC
OR HOMOLYTIC SUBSTITUTIONS

When studying metal atom exchange in the acetylene quasi-complexes formulated as metal chlorovinyls, Borisov and the author found that the chlorovinyl group retained its configuration during the reactions. Some of them, e.g.,



were electrophilic, others, such as the exchange involving tin dichloride,



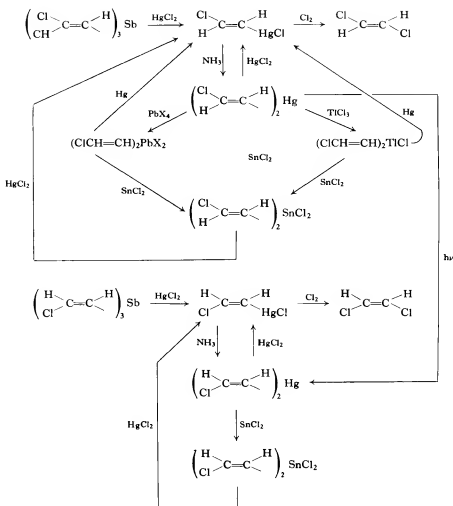
were homolytic. By 1945 we had accumulated enough evidence to suggest the rule: "The configuration (cis or trans) at an olefinic carbon atom is retained during electrophilic or homolytic reactions occurring at that atom." This was reported in 1945 (126). The scheme (p. 26) is taken from our paper published in *Dokl. Akad. Nauk SSSR* in 1948 (127, 128).

The rule was quickly confirmed. *cis* or *trans*- β -Chlorovinylmercury chloride treated with radioactive $^{203}\text{HgCl}_2$ rapidly produced the ^{203}Hg -mercurated chlorovinylmercury chlorides but the configurations were strictly retained (129).

The remarkable reaction discovered by Reutov, the fast exchange of bis(chlorovinyl)mercury with metallic ^{203}Hg , helped us to show that this apparently homolytic process involved fast insertion of ^{203}Hg and complete retention of the configuration (129).

Later, in collaboration with Borisov, we extended the rule to cover a wider class of organometallics, *cis*- and *trans*- $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{M})\text{C}_6\text{H}_5$ and *cis*- and *trans*- $\text{CH}_3\text{CH}=\text{CHM}$, where M is Li, Hg, Tl, Sn (130-132). The cycles of electrophilic and homolytic reactions performed did not reveal any exception to the rule, which was also shown to be true when applied to the reactions of *cis*- and *trans*-propenyllithium with typical organic compounds, i.e., aldehydes, ketones, and CO_2 (133, 122).

When we were undertaking this work NMR spectroscopy had not been discovered. Later, reinvestigating the compounds using NMR, we found



that the starting *trans*-chlorovinylmercury chloride and all metal *trans*-chlorovinyls obtained therefrom were stereochemically pure, whereas *cis*-chlorovinylmercury chloride contained some hard-to-remove *trans* isomer (135).

Thus we needed pure *cis*-chlorovinylmercury chloride in order to repeat the reactions using the NMR technique. The new results obtained did not change the conclusion made by us earlier (136).

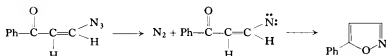
After the retention rule had been verified for reactions involving an olefinic carbon, we thought it necessary to develop the work in the following directions: We wanted to elucidate, first, the electrophilic substitution mechanism (at that time unknown) at a saturated tetrahedral carbon and, second, the nucleophilic substitution mechanism (also unknown in 1947–1948) at an olefinic carbon. The second problem was started earlier but resolved later than the first one. Two diastereomeric L-menthyl α -bromo-mercury phenylacetates were prepared (137) from menthyl α -bromophenylacetate and metallic mercury through a procedure suggested by Reutov (138). The ammonia symmetrization of each of the isomers gave mercury-bis(L-menthyl)phenylacetates which retained the configuration at the asymmetric carbon carrying the mercury atom (139). The reverse reaction of the mercury bis ester with mercury bromide was accompanied by racemization, but only if the reaction mixture was heated. On cooling the mixture, this artifact could be eliminated and the reaction $R_2Hg + HgBr_2$ shown not to disturb the configuration at the asymmetric tetrahedral carbon (137, 139–141) attached to the mercury. This area of research was extensively developed later by Reutov and his disciples, who discovered both the S_E2 kinetics and the fact that the reactions might occur as S_E1 substitutions if dimethyl sulfoxide was used as the solvent. In the latter case, racemization did occur.

The second problem was resolved in collaboration with N. K. Kochetkov and Rybinskaya, who studied alkyl and aryl β -chlorovinyl ketones whose chlorine atoms are readily substituted by nucleophiles. These compounds were both our disappointment and delight. Actually, *cis* and *trans* isomers of the compounds were unknown at that time (in 1949–1950), so the nucleophilic substitution stereochemistry was inaccessible. Moreover, the chlorine (or another group taking its place in a β -chlorovinyl ketone) reacted in a complicated manner, substitution being accompanied by addition at the double bond. This posed a difficult problem as to when the substitution is a primary reaction and when it is the result of an addition–elimination process. On the other hand, the charm of β -chlorovinyl ketones was that they provided real “open sesame” to organic synthesis, which for a long time led us away from our stereochemical problem. This branch is pure organic chemistry but it is worth mentioning because it is somehow entangled in our organometallic research. Here I will limit myself to the substitution stereochemistry, because *cis*- and *trans*- β -chlorovinyl ketones were isolated first not by us but by Italian authors (142) who also carried

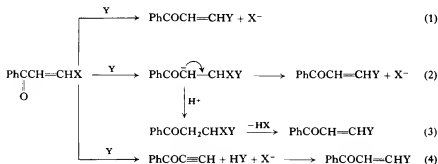
out some early investigations into the stereochemistry of nucleophilic substitution. The Italian authors studied the stereochemistry of exchanges of many β -chlorovinyl ketones with one of the stereoisomers. The retention of configuration in both *cis* and *trans* isomers was verified with thiophenolate only. We used phenyl *cis*- and *trans*- β -chlorovinyl ketones to obtain stereoisomeric $\text{ArCOCH}=\text{CHSO}_3\text{H}$ (143), $\text{ArCOCH}=\text{CHSO}_2\text{C}_6\text{H}_5$ (144), and $\text{ArCOCH}=\text{CHCN}$ (145), and to study nucleophilic substitutions therein. The most appropriate nucleophile was azide anion. We found that *trans*-azidovinyl aryl ketones were more or less stable and gave the aroyl acetonitriles when heated in DMF,



while the *cis* isomers lost nitrogen, undergoing the isoxazole ring closure, which was very useful.

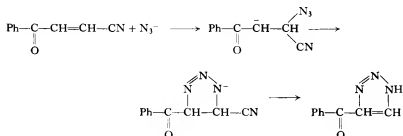


A priori, a nucleophile (Y) can attack an olefinic carbon according to four mechanisms:



All four proposals agree with the second-order kinetics usually observed. Mechanism (3) cannot be valid because it requires that the same stereoisomer be formed, whatever the nature of the initial isomer, whereas *cis* and *trans* isomers were shown experimentally to give the different products. Mechanism (4) was refuted by the fact that chlorovinyl ketones, $\text{PhC(O)C(CH}_3)=\text{CHX}$, which cannot lose HX, undergo nucleophilic substitution of the group X in precisely the same manner as do the ketones

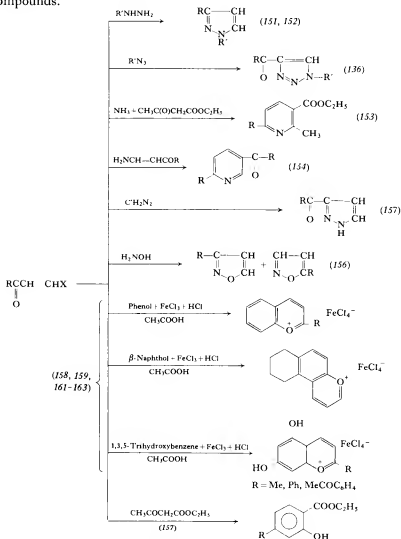
PhC(O)CH=CHX . As for mechanisms (1) and (2), good evidence in support of the second one is the striking fact that the reaction stereochemistry (N_3^- taken as the nucleophile) depends on the leaving group X. If X is Cl, Br, $\text{N}^+(\text{CH}_3)_3$, or NO_2 , then the entering N_3^- will not disturb the configuration. If X is SO_2Ph , however, the *cis* as well as the *trans* isomers will give the same mixture, in which the stable phenyl *trans*- β -azidovinyl ketone predominates. Finally, if X is CN^- or SO_3^- , the reaction follows the same course, complicated by ring closure, irrespective of the geometry of the starting compound:



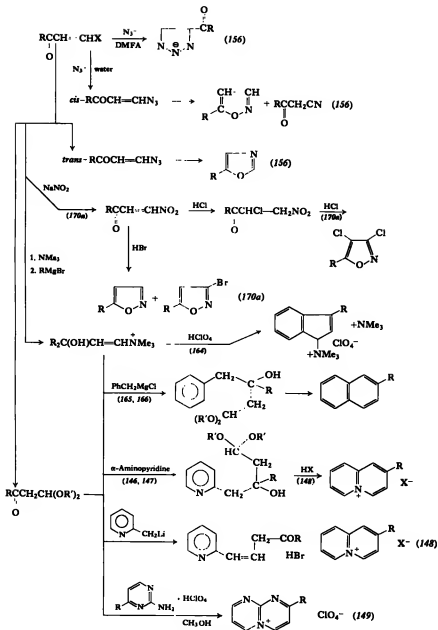
To sum up, nucleophilic substitution at an olefinic carbon (at any rate, at the sharply electrophilic one, as in β -substituted vinyl aryl ketones) involves addition of a nucleophile followed by formation of the PhC(O)CHCHXY^- anion, whose fate depends on the rate at which the group X^- leaves the molecule. If X^- leaves the molecule as soon as Y^- attacks, or almost so, then the configuration is retained [X is Cl, Br, $\text{N}^+(\text{CH}_3)_3$, NO_2]. If X^- is released slowly, then rotation around the σ -bond axis will take place to give the thermodynamically stable isomeric mixture in which the more stable *trans* isomer predominates. Finally, in our case when the nucleophile is N_3^- , if X leaves the molecule very slowly (CN^- , SO_3^{2-}), dipolar ring closure can occur to produce the 1,2,3-triazole system (146–150).

XI **CYCLIC COMPOUNDS THROUGH** **β -CHLOROVINYL KETONES**

The accompanying scheme illustrates some of our syntheses with these compounds.



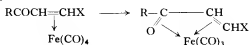
The Transformations of β -Substituted Vinyl Ketones

The Transformations of β -Substituted Vinyl Ketones (continued)

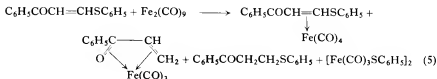
β -Chlorovinyl ketones were also used to show how CO and X compete for the orientation of the nucleophile Y, in the system RC(O)CH=CHX where X is NO_2 , $\text{SO}_2\text{C}_6\text{H}_5$, CN, or COOH (150a).

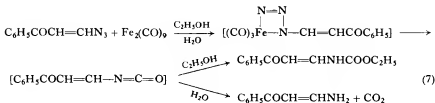
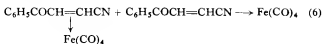
This synthetic work began in collaboration with N. K. Kochetkov and Rybinskaya as early as 1949, and was later (since 1956) applied to the synthesis of open-chain or cyclic π -complexes of β -X-vinyl ketones with a transition metal as heteroatom [Nesmeyanov, Rybinskaya, Rybin, and others (167-170)].

We were able to study the complexing ability of RCOCH=CHX qualitatively as a function of the substituent X (171-176). The reaction with $\text{Fe}_2(\text{CO})_9$ helped show that the π -complexes did not form in the case of either strongly electron-donating [e.g., $\text{X} = \text{N}(\text{C}_2\text{H}_5)_2$] or strongly electron-withdrawing ($\text{X} = \text{NO}_2$) substituents. The starting β -dimethylaminovinyl ketone could be recovered from the reaction mixture, while the nitro compound readily produced a polymer containing a nonstoichiometric percentage of iron. Stable π -complexes were obtained from RCOCH=CHX when X is H, Cl, COR, COOR, or SO_2R . The π -antibonding orbital energies calculated when $\text{X} = \text{NR}_2$, Cl, or NO_2 showed that the energy might be too high to allow for formation of the β -aminovinyl complex and too low with β -nitrovinyl ketone. The formation of the polymer in the latter case may be explained by assuming that the electron is completely transferred from the metal to the ligand, hence the anion-radical $(\text{RCOCH=CHNO}_2)^{\cdot-}$ is formed, which may initiate polymerization. The complexes $(\text{RCOCH=CHX})\text{Fe}(\text{CO})_4$ were shown to retain the initial configuration of the ligand, which was positioned equatorially in the complexes, and to diminish the ability of the β -substituent ($\text{X} = \text{Cl}$) to nucleophilic exchange. Also, the tetracarbonyl complexes readily gave the heterocyclic tricarbonyls.

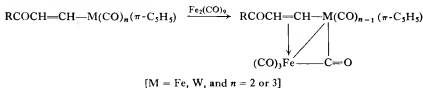


The nature of the β -substituent sometimes affected the course of the reaction, e.g.,

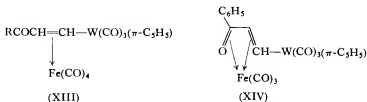




A special case was the reaction of β -substituted vinyl ketones whose β -substituents were $\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ or $\text{W}(\text{CO})_3(\pi\text{-C}_5\text{H}_5)$. The starting σ -complexes were synthesized by keto-vinylating the metal carbonyl anions (177, 178). The σ -complexes interacted with $\text{Fe}_2(\text{CO})_9$ to give novel binuclear complexes containing the M—M group bonded by both σ - and π -bonds to the same ligand.

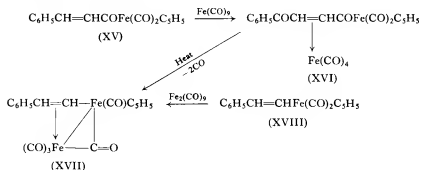


The formation of the binuclear complexes was shown to be affected both by the nature of the metal and by the σ -bonded ligand. The Fe—Fe, σ, π binuclear complex was the sole product (178) of reaction, while the Fe—W complex was isolated together with two side products, (XIII) and (XIV) (179).



The vinyl group of the initial σ -complex must be directly attached to the metal atom, otherwise the desired complex will not form. Interestingly, the

cinnamoyl compound (XV) gave complex (XVI), which, on heating gives the σ, π -binuclear complex (XVII) from which, however, the ketone CO group had been eliminated.



Note that the same σ, π -binuclear complex (XVII) may be obtained through a one-step synthesis from (XV) or through an independent synthesis from (XVIII) (180).

β -Iodovinyl ketones were also used to synthesize organomercurials. A homolytic reaction with mercury metal gave us a number of compounds such as $\text{RC}(\text{O})\text{CH}=\text{CHHgI}$, where R is CH_3 , C_6H_5 , etc., compounds which should be included with the vinyl organometallics synthesized in collaboration with Borisov earlier. They are described in the following section (Nesmeyanov, Rybin, Rybinskaya, Kaganovich).

XII

NON-TRANSITIONAL-METAL VINYL ORGANOMETALLIC COMPOUNDS

The quasi-complex compounds, as well as the complexes discussed above, led us into a domain which was nearly terra incognita at that time, namely, the substituted (β -chloro, β -alkyl, β -keto) vinyl organometallics. Thus, the simplest of metal vinyls became the objective of our work, and the vinyl, isopropenyl, propenyl, and styryl derivatives of elements such as Hg, B, Tl, Ge, Sn, Si, P, As, Sb, and Bi were studied in collaboration with Freidlina and Borisov. Apart from the procedures mentioned in Section V, vinyl-lithium and vinyl Grignard compounds were used for the synthesis. Note that the highest valence alkenyl derivatives of the type R_5Sb were reported by us (181-205).

Also, we performed a thorough study of the addition of organometallic hydrides (e.g., R_2SbH , R_3SnH) to organometallic acetylides, $R_2SbC\equiv CH$, $R_3SnC\equiv CH$, $R_3SiC\equiv CH$, and obtained a number of 1,2-dimetallated ethylenes, e.g., $R_2SbCH=CHSbR_2$, $R_3SnCH=CHSnR_3$, $R_2SbCH=CHSnR_3$, and even trimetallic derivatives, $(C_4H_9)_2Sn[CH=CHSn(C_4H_9)_3]_2$. The addition, as a rule, yields trans isomers.

XIII

TRANSITION METALS AND METAL CARBONYLS

Since 1939 I have come into closer contact with the organometallic chemistry of transition metals than I did during my first attempts to arylate $Fe(CN)_6^{4-}$. My attention was attracted to the paper by Job and Cassal, who synthesized chromium, molybdenum, and tungsten carbonyls by a simultaneous reaction of the halides with carbon monoxide and Grignard compounds.

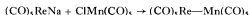
As an organic chemist I was well aware of the reducing properties of Grignard compounds. I thought, contrary to the opinion of the authors cited, that their reaction depended on the Grignard reactant acting as nothing more than a reducing agent. Indeed, we [Nesmeyanov, K. A. Kocheshkov, Anisimov, and others (206, 207)] verified that the Grignard compound might be successfully replaced by a reducing agent such as zinc powder, the yield of the carbonyl being 70% for tungsten, 46% for molybdenum, and 22% for chromium. The reaction was carried out in ether or acetone in an autoclave (CO, 100 to 120 kg/cm²) (206, 207). Later we obtained chromium carbonyl in 37% yield using pyridine containing $Mg + I_2$ or Na (209), and in 65% yield using ether containing lithium aluminumhydride as a reducing agent (208).

Tungsten or molybdenum hexacarbonyls were also found by us to be readily prepared from WCl_6 or $MoCl_5$, respectively, with iron pentacarbonyl. The yield was 75% with $W(CO)_6$ (210) and 30% with $Mo(CO)_6$ (211), higher pressures of CO being necessary in the latter case. As far as I know, our discoveries of 1939 were a starting point for the industrial preparation of metal carbonyls through the carbonylation of metal chlorides accomplished in various countries.

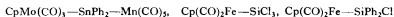
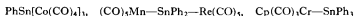
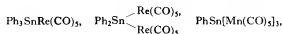
Our later investigations in collaboration with Freidlina and Chukovskaya (212) showed that metal carbonyls, especially iron pentacarbonyl, were

excellent catalysts for olefin telomerization, with CCl_4 or CHCl_3 or with SiCl_3H or R_3SiH .

The carbonyl work was continued in the 1960s when the ferrocene studies (see below) were extending the organometallic chemistry of transition metals. Here I will mention manganese-rhenium decacarbonyl (213) obtained by us through the reaction



This carbonyl, in which the metal-metal bond is covalent (Struchkov's and our data) attracted our attention to related compounds which could be readily prepared from salts such as $\text{NaMn}(\text{CO})_5$, $\text{NaRe}(\text{CO})_5$, $\text{NaCo}(\text{CO})_4$, or $\text{CpMo}(\text{CO})_3\text{Na}$. In collaboration with Anisimov, Kolobova, Khandozhko, Zakharova, Antonova, and others (214–226), we obtained many di- and polymetallic carbonyl-containing compounds through reactions of the salts with SiCl_4 , GeCl_4 , or SnCl_4 . Typical compounds obtained were



X-Ray investigation of some of the compounds was undertaken. Struchkov found that the metal-metal distance was equal to the sum of the covalent radii. The bond strength is rather high, even towards reactive reagents. Only chlorine or bromine were active enough to break the M—M' bond when added to the Cr—Sn , Mo—Sn , W—Sn , Mo—Pb , W—Pb , Mo—Sn—Mo , W—Sn—W , or Fe—Sn compounds. In $\text{Ph}_3\text{SnMn}(\text{CO})_5$ or $\text{Ph}_3\text{SnRe}(\text{CO})_5$, however, free halogen ruptured the phenyl-metal rather than the M—M' bond, forming not only $\text{X}_3\text{SnM}(\text{CO})_5$. Hydrogen halides abstracted just phenyl groups, forming not only $\text{X}_3\text{SnM}(\text{CO})_5$ but also $\text{X}_3\text{SnM}(\text{CO})_3\text{Cp}$ [from $\text{Ph}_3\text{SnM}(\text{CO})_3\text{Cp}$, $\text{M} = \text{Mo}$ or W]. One of the most interesting problems was the manner in which electronic effects were transferred along a biatomic (or longer) metal chain. We had studied this in the case of one metal (in ferrocene, see below). In the bimetallic systems, the transducers were groups attached to tin; their effects were observed as variations in the IR frequencies of the carbonyl groups attached to Mo or

W or as changes in the NMR chemical shifts of the cyclopentadienyl protons in the compounds $\text{Cp}(\text{CO})_3\text{MoSnX}_3$. The σ_i parameters turned out to fit the Hammett-Taft correlation best of all; hence the electronic effects of X were transferred through the bimetallic covalent chain in the same manner as electronic effects in saturated hydrocarbon chains, via an inductive mechanism (227-229, 236-240). Objects that are of interest for the study of transfer of electronic effects through a chain of atoms of metals were the clusters obtained by us (230-236) from $\text{CpM}(\text{CO})_4$ where $\text{M} = \text{Ta}, \text{Nb}, \text{V}$.

Acyl chlorides obtained from aromatic, heterocyclic, or dibasic aliphatic acids allowed us to obtain acyl derivatives from $\text{NaMn}(\text{CO})_5$ or $\text{NaRe}(\text{CO})_5$. Their decarbonylation gave the respective σ -aryl, σ -heterocyclic, or substituted-alkyl derivatives, allowing studies as to how a substituent influenced a CO group through a benzene ring (or an alkyl chain) and a metal bonded thereto (241-244).

XIV

FERROCENE¹ AND METALLOCENES

I was brought up to believe that transition metals cannot form stable organometallic compounds, i.e., alkyl, aryl, alkenyl, or similar derivatives. This belief, which goes back to Mendeleev, found so many confirmations that the rare exceptions (Pt) seemed to corroborate it. From time to time, I reproduced the so-called syntheses of organometallic compounds of scandium, of diarylcopper, and of diaryliron claimed in the literature, and the results were always negative (245, 246). So, the ingenious paper of Kealy and Pauson, who reported in 1951 the synthesis of dicyclopentadienyliron [stable up to 470° C (!)] sounded like a bolt from the blue. This undoubtedly heralded the advent of a new era in organometallic chemistry. Immediately, my co-workers in Moscow University were reoriented towards ferrocene investigations, as were also some of my co-workers in the Institute of Organo-Element Compounds organized by me in 1954. Woodward, Rosenblum, Whiting, and the same authors and Wilkinson, soon established the sandwich structure and the Friedel-Crafts acylation of ferrocene. They pointed out the aromaticity of the compound which, however, was a point of controversy between them and Fischer. Our first ferrocene paper, published in 1954 (247), reported other substitutions

¹ See references 247-341.

characteristic of aromatic and super-aromatic systems: mercuration (247), metalation with butyllithium (247) and with butylsodium (254), and the diazonium arylation (248) of ferrocene. Of course, the compound was very attractive to other investigators as well. Enraptured by the ferrocene avalanche, inorganic chemists were synthesizing other metallocenes, while organic chemists were extensively studying ferrocene. The Pauson discovery, when considered together with the Sidgwick rule, prompted me to think that dibenzenechromium and its homologs should exist, so I suggested to Vol'kenau (at that time she was with me as a post-graduate) the combination of benzene with a chromium salt reduced in *statu nascendi*, as in our synthesis of Cr, Mo, and W carbonyls. I could not realize that aluminum chloride was also necessary for the reaction to occur, otherwise I would have accomplished the Fischer synthesis of dibenzenechromium. I did not realize either that the Hein polyphenylchromium compounds reported as early as in 1920 were indeed diarene chromium compounds. As for ferrocene, sometimes we were somewhat ahead (the diazonium arylation, Pauson; lithiation, Benkeser), sometimes in the rear [sulfonation, Weinmayr (247)] of other investigators. We focused our attention on homologs of ferrocene, i.e., Friedel-Crafts alkylation by alkyl halides or olefins (248-251), reduction of acyl or alkylacyl ferrocenes (252, 253), reduction of ferrocenecarboxylic acids and reduction of dimethylaminomethylferrocene to methylferrocene (254-256). Good results were obtained with Friedel-Crafts alkylations using a reducing agent (257).

Ferrocene organomercurials were also used to prepare a number of other derivatives, namely, halogen-, sulfur-, or selenium-containing compounds, biferrocenyl, or triphenylmethylferrocene [Nesmeyanov, Perevalova, O. A. Nesmeyanova (258, 259)]. Lithiation or sodium metalation provided even more versatile reagents, the reactions being used by other investigators as well.

Of this research, I will mention here only aminoferrocene. We were very glad to obtain the compound through the Kocheshkov reaction of ferrocenyllithium and hydroxylamine *O*-ether [Nesmeyanov, Perevalova, Shilovtseva (260)]; later, we synthesized aminoferrocene via other paths (261, 262).

Our first ferrocene papers described one more reaction: the synthesis of bis(tetrahydroindenyl)iron through the acylation of ferrocene with succinic anhydride, reduction, then closure of the six-membered ring followed by reduction again. The compound was identical with that obtained by

Fischer from tetrahydroindene (253). In a similar manner, we obtained ferrocene analogs of anthrone and anthraquinone from ferrocene and phthalic anhydride.

Now let me come back to primary substitutions at the ferrocene nucleus. Together with Vil'chevskaya, we phosphorylated ferrocene and its derivatives to triferrocenylphosphine oxides (263, 264). An unusual reaction, discovered in collaboration with Perevalova and Yur'eva, was the direct cyanation of ferrocene with hydrocyanic acid in the presence of ferric chloride (265, 272). Initially, cyanide attacks the iron atom of the ferricinium cation, then the cyanide group transfers to the ring while the iron is simultaneously reduced. The reaction was termed by us as the ricochet (from the metal to the nucleus) substitution; it may be applied to many substituted ferrocenes and to the ruthenocenium cation (273), and it is now the simplest route to ferrocene carboxylic acids through their nitriles. Further, ferrocene was studied in acid-medium reactions with oxo compounds. With aldehydes (274), the reaction was complicated by the transformation of ferrocenylalkyl carbinol formed initially via the carbonium ion, followed by transformation to a radical which, in its turn, was coupled to 1,2-bis-(ferrocenylalkyl)ethane (275). The reaction with acetone led to 2,2-di-ferrocenylpropane (276).

Very soon we could deduce that electrophilic substitution rules are transformed when the benzene nucleus is replaced by the ferrocene nucleus. Actually, substituents of the first kind (ortho and para orientants) direct an electrophile to the same cyclopentadienyl ring while those of the second kind (meta orientants) direct electrophiles to the other. We showed this to be true for ricochet substitutions as well. However, the first/second type boundary, as determined for ferrocene, differs from that found in the benzene series, the electron-accepting type embracing an essentially greater number of substituents in the former case (see below).

The simplest electrophilic substitution is deuteration in acid media. Kursanov, Setkina, Nefedova, Kislyakova, Kochetkova, and the author showed that the exchange rates (in trifluorodeuteroacetic acid) were 5300:5.0:2.6:1 for ferrocene, acetylferrocene, 1,1'-diacetylferrocene, and toluene, respectively, while they were 41.2:9.6:9.6:1 in 1,1'-diethylferrocene, ethylferrocene, methylferrocene, and ferrocene, respectively. Finally, the ratio was 1:0.0007:0.33:23.3:50.8 for ferrocene, chloroferrocene, phenylferrocene, methoxyferrocene, and ethylferrocene, respectively (277-279).

NMR spectroscopy allowed us to discern between the rates characterizing deuteration at the free and at the substituted ring. The ratio was 5:14 for ethylferrocene and 2.4:12 for *tert*-butylferrocene (the rate characterizing the unsubstituted ferrocene is arbitrarily taken as unity) (280).

Later Kursanov and Setkina found that in ferrocene interaction between substituent and nucleus was quite different from that in benzene. This is especially true for donor substituents such as C_2H_5 or CH_3O , which accelerated the exchange rate a few orders in benzene but only a few times in ferrocene.

Ferrocenyl considered as a substituent on a benzene ring is a donor (281), stronger even than methyl. The mutual effect of the rings was studied in ferrocenylbenzene. Ferrocenyl in ferrocenylbenzene was a strong ortho, para-orienting substituent and directed the nitro group to the para position of the benzene ring (282).

Strong electron donation by the ferrocenyl group was also substantiated by the fact that K_a values found for *p*-ferrocenylbenzoic acid or *p*-ferrocenylphenol were higher, while those for ferrocenylaniline lower, than the K_a values of the unsubstituted compounds. The ring-to-ring transfer of the substituent effect was studied for the first time by Nik. A. Nesmeyanov, my son, who measured dissociation constants of the acids $XC_5H_4FeC_5H_4COOH$ where X was one of various electron-withdrawing groups or electron-donating alkyls (283). It was concluded that the X group operated in the same manner as in X-meta-substituted benzoic acids, mainly through an induction mechanism. Another group of my co-workers (Perevalova and Gubin; also Grandberg and Zharikova) studied the effects of substituents more extensively (284-289). We showed that the logarithmic constants of dissociation of X-substituted ferrocenecarboxylic acids correlated well with σ_m or with σ_I , though $\log K_a$ of halogenated ferrocenecarboxylic acids deviated somewhat from the correlation using σ_I .

However, the transannular effect of the substituents was shown to operate essentially through an inductive mechanism. The effects were studied most extensively with the redox potentials of the X-substituted ferrocene versus the X-substituted ferricinium system. The potentials of the ferrocene derivatives offer a parallel to the activity of the ferrocene nucleus as a function of the substituents. Alkyl ferrocenes are oxidized more readily than ferrocene and they are more active in their electrophilic substitutions. Halogens, $COOH$, $COOCH_3$, $NHCOCH_3$, $HgCl$, CH_2OH , C_6H_5 , to say nothing about $RC(O)$ and CN groups, are electron acceptors

towards ferrocene and they hinder both electrophilic substitutions and oxidation.

The Hammett-Taft analysis of the redox potentials gave a good correlation using σ_p^0 parameters. Also, the dependence was additive for the disubstituted ferrocenes,

$$\log (K_{XY}/K_H) = \rho_0 \sum \sigma_p^0,$$

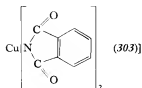
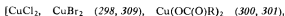
hence the substituents X and Y did not interact. The correlation analysis showed us that the XC_5H_4 ring interacted with the ferrocene iron atom in the same manner as X interacts with carboxyl in the $p\text{-X-C}_6\text{H}_4\text{CH}_2\text{COOH}$ system, where the CH_2 group discontinues the conjugated chain (σ_p^0 parameters were used). Hence, the ferrocene aromatic nucleus does not transfer the T-effect to the iron and this is even more true as regards the other ring.² The hindering effect of the ferrocene nucleus on conjugation of the heteroannular substituents was also demonstrated by studying dissociation constants of substituted ferrocenecarboxylic acids, integral IR intensities of the unsubstituted ring (284, 285, 290), overall IR intensities of the CH bonds, and the electron spectra. At the same time, the inductive conductivity of ferrocenyl ($\rho_i = 1.385$) and phenyl ($\rho_i = 1.464$) nuclei are close (284).

The ferrocene nucleus proved to be absolutely unable to undergo the rearrangements characteristic of the benzene ring, so the Claisen rearrangement of allyl ferrocenyl ether (291), the benzidine rearrangement of hydrazoferrocene (294–296), and the Sommelet rearrangement in the ferrocene series were all unsuccessful.

Also, reaction site transfer observed with benzene was found not to occur with ferrocene. For example, ferrocenylmethyl lithium reacted with formaldehyde to give β -ferrocenylethanol, not 2-methylolmethylferrocene. With CO_2 , ferrocenylacetic acid was formed rather than 2-methylferrocenecarboxylic acid (297). This passivity may also be associated with the fact that ferrocene, a non-alternant aromatic system, cannot transfer the T-effect.

An extremely versatile synthetic method depended on substitution of ferrocenylboric and ferrocenylenediboric acids, the compounds obtained from boric ester and lithium- or dilithiumferrocenes by Sazonova, Drozd, and the author (298, 299). The boric group is readily replaced by cupric (see top of p. 42) or cuprous $[\text{CuCN}, \text{CuC}\equiv\text{CR}]$ salts. This was the simplest route to mono- or disubstituted halogenated ferrocenes, oxy-ferrocenes and

² This applies to electron-withdrawing substituents.



their esters (300, 302, 304, 306), aminoferrocenes (303, 307), and various heterocyclic ferrocenes (305). Ferrocenylboric acids treated with a solution of silver oxide in aqueous ammonia gave the silver-substituted ferrocene and, further, diferrocenyl and terferrocenyl were also synthesized (308–310).

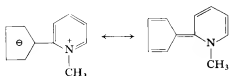
Chlorine or bromine is as inactive in chloro- or in bromoferrocene as it is in the benzene analogs. We found, however, that copper salts facilitated the nucleophilic exchange and the bromine atom of bromoferrocene could be substituted by OC(O)R , NR_2 , phthalimide (304, 311), aryls, or heterocyclyls (312) under the action of either ArMgX in the presence of CuX (Ar is aryl or heterocyclyl) (313) or of Ar_4BK plus CuX . This line of work produced ferrocenol and its esters, and one more method of obtaining ferrocenylamine and its acylated (314), alkylated (315), and arylated (307, 314) derivatives. Copper exchange using the azide anion gave ferrocenyl azide (316), the reduction of which gave one more route to ferrocenylamine (316). Ferrocenyl azide with various RMgX reagents yielded the triazenes (317), the acidolysis of which gave us ferrocene diazonium salts which would be hard to prepare through any other procedure. We also studied the reactions of the diazonium salts obtained, e.g., diazo coupling (318), and also prepared ferrocenylene diazide and 1,1'-ferrocenylenediamine.

A series of secondary or tertiary aliphatic and aromatic amines akin to ferrocene (307, 314, 315), and its azo and hydrazo derivatives (319), were also synthesized and studied. Basicities of amines of the ferrocene series were reported in (292, 293).

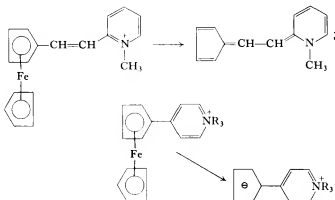
The ferrocenylammonium derivatives $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{N}^+\text{R}_3$ were shown to photolyse to the cyclopentadienylides (320, 321).



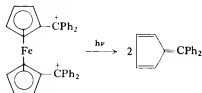
Methiodides of α -pyridylferrocene (320) or of α -quinolylferrocene (320) underwent the same reaction, leading to ylides of the type:



Photolysis occurs even if the positively charged center is separated from the nucleus by a conjugated chain (321), e.g.,



The photolysis proceeds with carbonium systems as well, and leads to the fulvenes, for instance (322-324)



Many authors noted that an α -carbonium center was stabilized in ferrocene derivatives. Richards believed that such a center might interact directly with the iron. We were also dealing with the behavior of the α -carbon of a side chain attached to ferrocene. For synthesis purposes we studied the anion-exchange reactions of ferrocenylmethyltrimethylammonium salts and thus obtained and studied ethers (325) and esters of ferrocenylcarbinol, their sulfur-containing analogs (326), and various amines. Grignard compounds made ammonium salts exchange their trimethylamino group for the group of the Grignard reagent. Lithium aluminohydride led to

methylferrocene. Ferrocenylmethyl alkyl ethers, in their turn, were decomposed by lithium to give ferrocenylmethylolithium (327), which allowed us to perform a number of other syntheses. It is interesting to compare ferrocenylmethyl with its benzyl analog. The cation $[C_5H_5FeC_5H_4CH_2N^+(CH_3)_2(CH_3Ph)]$ was hydrolyzed to ferrocenylcarbinol par excellence (328), the mechanism being probably S_N1 . Thus, ferrocenylmethyl cation is more stable than benzyl cation. The ammonium cation above, if reduced by sodium amalgam, gives predominantly toluene. This shows that the benzyl radical is more stable than ferrocenylmethyl radical (329).

The Stevens rearrangement of the same ammonium salt led to $C_6H_5CH[N(CH_3)_2]CH_2C_5H_4FeC_5H_5$, hence an anionic center is more stable when positioned alpha to phenyl as compared with ferrocenyl (330).

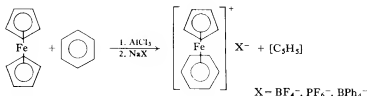
This agrees with the conclusion we had arrived at, viz., that ferrocene differs from benzene in that the latter is equally sensitive to electron-donating and electron-accepting substituents, while ferrocene is susceptible to the electron-accepting ones only.

Hydrolysis of ferrocenylmethyltrialkylammonium salts (328), or the action of Li or Mg organic compounds on ketones and nitriles of the ferrocene series, led to ferrocenyl- (331, 332) and triferrocenylcarbinols (333, 334) and the respective carbonium salts. Electrophilic reactions of these carbonium cations were studied. These included the reaction with anions (among them, bidentate species), the attack at aromatic rings (335) and at pyridine (336, 337), and the fulvene formation mentioned above, e.g. the synthesis of diferrocenylfulvene from triferrocenylcarbonium salt (338). Triferrocenylchloromethane was shown to give a surprisingly stable complex with hydrogen chloride, the reactions of the hydrochloride (339) being described in reference (340). Diferrocenylcarbonium salts gave the hydrochlorides as well (341).

XV

LIGAND EXCHANGE IN FERROCENE. ARENE CYCLOPENTADIENYL DERIVATIVES OF IRON

In collaboration with Vol'kenau, Bolesova, Shilovtseva, Isaeva, and Sirotkina we found that one of the cyclopentadienyl groups of ferrocene could be replaced by an arene ligand, whereby the arene cyclopentadienyl iron cation was formed (342):



The catalyst may be AlCl_3 , AlBr_3 , or ZrCl_4 .

Electron-donating substituents attached to either the arene or the cyclopentadienyl groups facilitated the reaction, while the electron-accepting ones hindered the exchange reaction. Monosubstituted ferrocenes containing electron donor substituents underwent exchange of the substituted ring whereas electron acceptors caused exchange of the unsubstituted nucleus (343). The reaction was found to occur with aromatic hydrocarbons, aromatic ethers, their sulfur analogs (ArSAlk), halides (ArHal ; Hal is F, Cl, Br), aromatic amines (primary and secondary), and $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$ (342–347). Moreover, di- and monosubstituted ferrocenes could enter into the reaction, the substituents being Alk, Ar, Cl, CH_3CO , CN (343).

As a result, a great number of iron arene cyclopentadienyls were obtained.

The cationic nature of the compounds makes them unable to undergo any electrophilic substitution.

In contrast, nucleophiles react with the cations quite easily. The isomeric halides $[\text{HalC}_6\text{H}_5\text{FeC}_5\text{H}_5]^+\text{BF}_4^-$ (Hal is F, or Cl) and $[\text{C}_6\text{H}_6\text{FeC}_5\text{H}_4\text{Cl}]^+\text{BF}_4^-$ readily exchanged their halogens for nucleophiles such as AlkO^- , ArO^- , AlkS^- , ArS^- , NH_2^- , NHR^- , CN^- , and phthalimide anion (346–349).

Kinetic investigations (350) showed that chlorine in $[\text{ClC}_6\text{H}_5\text{FeC}_5\text{H}_5]^+\text{BF}_4^-$ was almost as active as in 2,4-dinitrochlorobenzene, while the halogen attached to the five-membered ring was about three orders less active.

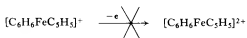
The halogen activity fits well the data on acidity and basicity of the arene (cyclopentadienyl) iron acids and amines.

All acids of the type $[\text{HOCC}_6\text{H}_4(\text{X})\text{FeC}_5\text{H}_5]^+\text{BF}_4^-$ proved stronger than the respective benzoic acids. The acid $[\text{C}_6\text{H}_6\text{FeC}_5\text{H}_4\text{COOH}]^+\text{BF}_4^-$ was stronger than the ferrocenecarboxylic acids, while $[\text{HOCC}_6\text{H}_5\text{FeC}_5\text{H}_5]^+\text{BF}_4^-$ was stronger than $[\text{C}_6\text{H}_6\text{FeC}_5\text{H}_4\text{COOH}]^+\text{BF}_4^-$ (351, 352).

Isomeric amines of this kind were, in contrast, weaker bases than aniline and ferrocenylamine, respectively. The amine $[\text{C}_6\text{H}_6\text{FeC}_5\text{H}_4\text{NH}_2]^+\text{BF}_4^-$ was a stronger base than $[\text{H}_2\text{NC}_6\text{H}_5\text{FeC}_5\text{H}_5]^+\text{BF}_4^-$ (353). The amine

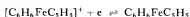
containing NH_2 on the cyclopentadienyl ring could be diazotized and the diazonium salt isolated and coupled with β -naphthol (354).

Although arene-cyclopentadienyl iron cations are isoelectronic with ferrocene and contain a formally bivalent iron, they are extremely stable towards oxidation. Even such reagents as $\text{H}_2\text{O}_2/\text{NaOH}$, $\text{CrO}_3/\text{H}_2\text{SO}_4$, and KMnO_4 failed to oxidize them to the desired doubly-charged cation (351).



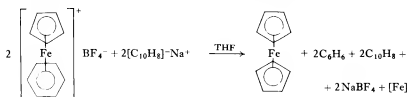
This resulted in a synthetic procedure, namely, the oxidation of alkyls attached to the arene or cyclopentadienyl ring of the π -complexes to give carboxylic acids of the arene cyclopentadienyl iron series (346, 347, 351).

Polarography (the same authors as above, and Gubin and Denisovitch) showed (355) that arene-cyclopentadienyl iron cations were able to undergo a one-electron reduction,



the product being an extremely unstable paramagnetic species whose life-time was seconds.

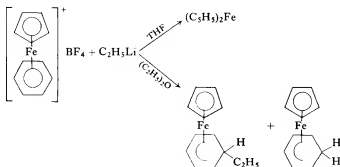
The chemical reduction (Na/Hg , sodium naphthalide) revealed that the primary product disproportionated to give ferrocene and an arene (356).



Various reducing agents such as Na , Na/Hg , $\text{C}_{10}\text{H}_8\text{Na}$, Mg/Br_2 , AlkLi , AlkMgBr , $\text{C}_5\text{H}_5\text{Na}$, and also the nucleophiles $\text{C}_2\text{H}_5\text{ONa}$ and H_2NNa , were shown to induce this reaction (357, 358).

The interaction of organolithium and -magnesium reagents with arene cyclopentadienyl iron cations depended significantly on the solvent. In tetrahydrofuran, the main reaction was disproportionation and formation of ferrocene. In ether, nucleophilic addition to the arene ligand occurred, affording cyclohexadienylcyclopentadienyliron. The adding species was either the organic group of the organolithium agent or a hydrogen atom which was abstracted from one of the reactants (most probably, from the same

group). For example, C_2H_5Li reacted with $[C_6H_6FeC_5H_5]^+BF_4^-$ in the following way (359):



Both the formation of ferrocene and the formation of cyclohexadienyl-cyclopentadienyl derivatives of iron might be supposed to involve the same intermediate, the product of one-electron reduction of the initial cation.

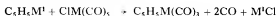
Reduction of arene cyclopentadienyl iron cations was another interesting aspect of the research.

Naphthalenecyclopentadienyliron tetrafluoroborate, when reduced with sodium amalgam under very mild conditions (at $-20^\circ C$), gave the product of exchange of arene for another ligand (arene, CO). The reaction does not work in the absence of a reducing agent, hence it may also be supposed to proceed via the reduction of the cation and formation of the intermediate (359).

XVI

CYCLOPENTADIENYLMANGANESE TRICARBONYL AND CYCLOPENTADIENYLRHENIUM TRICARBONYL

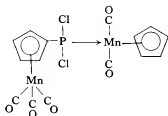
Fischer, Geiss, and others showed that cyclopentadienylmanganese tricarbonyl (CTM) possessed an extremely "aromatic" ring. We thought it useful to apply the reactions discovered by us for ferrocene to this molecule and to its rhenium analog (CTR). We succeeded in obtaining the compounds through the reaction (360-363)



We found that Friedel-Crafts alkylation of CTM or CTR was possible, as well as acylation (364). In this manner, a number of CTM homologs were obtained (365–367). Dehydration of the CTM alcohols gave us the alkenyl derivatives. Reduction of the acylated derivatives and use of Grignard reactions were a source of secondary and tertiary alcohols whose dehydration gave us the alkenyl derivatives [Nesmeyanov, Anisimov, Kolobova, Zlotina (368, 369)].

As for the primary substitutions in CTM or CTR, mercuration, metalation by butyllithium [Nesmeyanov, Anisimov, Valueva (370); the same authors and Makarov (371, 172)], chloromethylation by paraformaldehyde and HCl (373), a number of nucleophilic substitutions of the chloromethyl derivative (374, 375), and the Sommelet transformation of the chloromethyl derivative to the aldehyde were all performed.

The aldehyde was typically aromatic; it gave the hydramide in its reaction with ammonia, and underwent the Cannizzaro reaction. CTM was phosphorylated by PCl_3 in the presence of aluminium chloride to give



the reaction being complicated by complex formation (376).

Lithiated CTM or CTR was used for a number of syntheses, e.g., CTM or CTR boric acids were obtained, the ferrocene analog of which had been shown to be so useful for the synthesis of ferrocene derivatives (377). However, CTM and CTR boric acids were very soon shown to differ from ferrocenylboric acid and resemble phenylboric acid. The $\text{B}(\text{OH})_2$ group was readily substituted by HgCl on treatment with HgCl_2 , while Cl or Br entered only after the initial acid had been refluxed with CuCl_2 or CuBr_2 in water for hours. The yields of chloro- or bromo-CTM were, however, fairly good. In contrast, with copper acetate nothing but CTM and bis-CTM were isolated (378). The halogenated CTM and CTR were also obtained through the reaction of $(\text{CTM})_2\text{Hg}$ or $(\text{CTR})_2\text{Hg}$ with CuCl_2 or CuBr_2 (377).

α -Oxo derivatives of CTM gave vinyl derivatives and their homologs.

The vinyl derivative was converted to ethynyl-CTM by reaction with bromine followed by HBr elimination. The double bond of vinyl-CTM turned out to be much less active than that in the ferrocene analog as regards electrophilic addition. Also, the stabilization of an α -carbonium center, the phenomenon characteristic of ferrocenyl cation, was not found in the manganese compound (379).

Substitutions in the CTR were studied in collaboration with Anisimov, Kolobova, Makarov, and Baryshnikov. We sulfonated (380) and mercurated (380) the compound, and metalated it (372) with butyllithium in THF. Lithiated CTR gave CTR-carboxylic acid (pK 4.73 in 50% aqueous ethanol at 25°C; cf. pK of CTM-carboxylic acid, 4.99). CTR boric acid was also prepared (377); it hydrolyzed even more easily than its CTM analog. Mercury-bis-CTR produced chloro- or bromo-CTR on treatment with CuX_2 (377).

The deuterium exchange in CTM and CTR performed in collaboration with Kursanov, Setkina, Kislyakova, and others (381) gave us very interesting information. The rate constant measured for CTM in CF_3COOH and H_2SO_4 was from 1.3 to 2 times that of benzene and 5 times that of CTR (the constant is orders higher for ferrocene) (382). In monoalkylated CTM derivatives the constant increased by a factor of 5 to 10, in dialkylated or trialkylated ones by a factor of 70 to 100. In other words, the increment was insignificant as compared with that in the benzene series [1.5 order for toluene, 7 orders for mesitylene (383)]. The regularity was the same as in ferrocene. In alkaline media (sodium alkoxide) CTM and CTR also exchanged their hydrogens for deuterium, the CTR:CTM constants ratio being 27 (384).

Certain readily accessible homologs of ferrocene prompted us to use them for the preparation of metal cyclopentadienyls containing a substituent on the ring (Nesmeyanov, Kochetkova, Materikova). Only first attempts have been made in this direction so far. We found that C_5H_5I or its homologs gave excellent yields of the metallocenes in the reaction with metal halides (385, 386). The abstraction of substituted cyclopentadienyls by lithium in ethylamine according to Trifan and Nicholas (387), followed by transformation of the lithium cyclopentadienyls to the thallium derivatives or by direct application of the latter cyclopentadienyls, enabled us to synthesize the homologs of cobalticene (388, 389), nickelocene (385), and also $(RC_5H_4)_2ZrCl_2$ and $(RC_5H_4)_2HfCl_2$ (390), and non-transition-metal cyclopentadienyls (385, 390) from the respective metal halides.

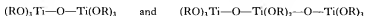
Dicyclopentadienylmercury, cyclopentadienylmercury halides, and cyclopentadienylmethylmercury studied *in situ* were assumed to be sandwich π -complexes (391-394). This was based on our IR and NMR investigations (NMR at $+35^\circ$ to -70°C) carried out in collaboration with Sheinker, Fedorov, Materikova, Kochetkova, and others.

XVII

ORGANOTITANIUM COMPOUNDS

In collaboration with Freidlina, Nogina and Brainina we started an investigation into titanium organic chemistry, namely, titanium alkoxides. Good methods were worked out for the synthesis of the compounds $(\text{RO})_n\text{TiX}_{4-n}$ where n is 1-4, and X is Cl or Br (395-404). The compounds $(\text{RO})_2\text{Ti}(\text{OR}')_2$ and $(\text{RO})_3\text{TiOR}'$ were also obtained and the properties of all compounds studied. For example, tetraalkoxytitanium compounds were found to induce the Tishtshenko condensations of aldehydes (395).

Trialkoxy derivatives of trivalent titanium were synthesized, and their interesting reactions, e.g., the oxidation to the dialkoxytitanium oxides, studied. For the first time, the low-alkyl polyalkoxy titanoxanes



and their halogenated derivatives were prepared (405).

Later, together with Nogina, Dubovitskii, and others, we studied titanium cyclopentadienyls. Mono and bis cyclopentadienyl derivatives of quadrivalent titanium, unlike ferrocene, were shown not to substitute at the nucleus (acylation, alkylation, mercuration, cyanation). On the other hand, titanium cyclopentadienyls were found to readily decompose under the action of nucleophiles, the activity of the $\text{Ti}-\text{C}_5\text{H}_5$ bond depending on the ligand. For example, the bond is broken under conditions as mild as ethanol treatment at 20°C in the case of $\text{C}_5\text{H}_5\text{Ti}(\text{OC}_2\text{H}_5)_3$ and $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{OCOCH}_3)_2$ (406). Consequently, we focused our attention on ligand exchange and the nature of the $\text{Ti}-\text{C}_5\text{H}_5$ bond.

A number of facile procedures were developed for the synthesis of mono and bis cyclopentadienyl derivatives of titanium, e.g., the $(\pi-\text{C}_5\text{H}_5)$ -trialkoxytitanium derivatives, $(\pi-\text{C}_5\text{H}_5)$ -titanium trihalides (406, 407-409), $(\pi-\text{C}_5\text{H}_5)$ -titanium internal complexes (409), triaroxytitanium cyclopentadienyls (410), compounds containing different groups (alkoxy, aryloxy,

acyloxy, halogens) attached to the metal (406–409, 411, 412), bis(cyclopentadienyl)titanium alkoxy halides (407, 408), and others.

The new syntheses and the properties of the compounds mentioned above or obtained in other ways enabled us to study the titanium–cyclopentadienyl bond as a function of the ligands.

We studied the series $\text{RTi}(\text{OR}')_n\text{X}_{3-n}$ ($n = 0-3$), where R is C_5H_5 (406–412), $\text{CH}_3\text{C}_5\text{H}_4$ (406), $\text{C}_5(\text{CH}_3)_5$ (409). R' is C_2H_5 (406–409, 412), iso- C_3H_7 (409), C_5H_5 (406, 411); and X is F (409), Cl (406, 407, 409, 411, 412), Br, or I (409). Several bis(cyclopentadienyl)derivatives were also studied. It was found that alcoholysis or hydrolysis of the compounds gave more cyclopentadiene the fewer electron-accepting halogen atoms were attached to titanium. The same was true for the reaction with a salt of bivalent iron to give ferrocene (406, 407, 410–415). Physical investigation of the compounds was also carried out: IR (409, 411, 416, 417), mass spectra (418), NMR (413, 414, 419), and electroconductivity measurements (413). The results combined with the chemical behavior, led us to conclude that the $\text{Ti}-\text{C}_5\text{H}_5$ π -bond polarity increases with decrease in electron-accepting ability of the ligands. The bond was also sharply affected by electron-donating methyls attached to the cyclopentadienyl ring. This was clearly demonstrated by alcoholysis (406) and by the reaction with Fe^{2+} (417), accomplished for the series $\text{RTi}(\text{OC}_2\text{H}_5)_3$ where R is C_5H_5 , $\text{CH}_3\text{C}_5\text{H}_4$, and $\text{C}_5(\text{CH}_3)_5$. Note that the rupture of the $\text{Ti}-\text{C}_5(\text{CH}_3)_5$ bond of $\text{C}_5(\text{CH}_3)_5\text{Ti}(\text{OC}_2\text{H}_5)_3$ occurred only under the action of sodium alkoxide on prolonged heating.

Also, the ligand effect as transferred through the titanium was studied by observing the activity of X in nucleophilic reactions of RTiX_3 , where R is C_5H_5 , $\text{CH}_3\text{C}_5\text{H}_4$, or $\text{C}_5(\text{CH}_3)_5$. For example, ethanolysis of various RTiCl_3 compounds under similar conditions showed that the yield of $\text{RTiCl}_2(\text{OC}_2\text{H}_5)$ decreased sharply with an increase of the number of methyls attached to the ring (415). The cyclopentadienyls containing donor substituents also affect the fluorine which is not directly bonded to titanium (mono and bis cyclopentadienyl *p*-fluorophenoxy derivatives of the metal) and the fluorine in trifluoroacetyl derivatives of cyclopentadienyl-titanium. As the number of methyls attached to the cyclopentadienyl increases, the ^{19}F NMR signals are shifted upfield (419).

In complexing solvents, monocyclopentadienyl derivatives differed in their properties from the bis(cyclopentadienyl) ones (419). The fluorine chemical shift was affected by the nature of the rings in the latter compounds

only. This may be associated with the coordination of the solvent to the metal, which may take place in the mono, but not in the bis derivatives, owing to the spatial hindrance displayed by two cyclopentadienyl groups.

Also, the transfer of electronic effects was studied in the cyclopentadienyl-titanium-ligand systems, viz. the $(\pi\text{-C}_5\text{H}_5)_2$ -ligand interaction, and the interaction of the ligand with the $\pi\text{-C}_5\text{H}_5\text{—Ti}$ bond.

The titanium research was somewhat ramified when Freidlina and Brainina started their zirconium and hafnium investigations. I took part in earlier stages of the work (420–423). The most promising result was the concept of “headlight bonds” suggested by Bocharov, Gambaryan, Brainina, and Freidlina (424).

XVIII

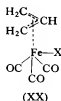
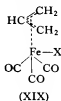
π -ALLYL COMPLEXES

Starting from our ferrocene investigations, we (Kritskaya and the author, in collaboration with Yu. Ustynyuk and Struchkov) studied π -allyl complexes of iron.

Metal π -cyclopentadienyls somewhat resemble the π -allyl complexes. Initially, when the nature of the metal-allyl bond was not sufficiently clear, the similarity was emphasized many times [see the review by E. O. Fischer (425)]. The similarity shows itself, for example, in the equal antisymmetric C—C stretching frequencies (1640 cm^{-1}), which indicate that the force constants, hence the bond orders, are close. The central π -allyl proton absorbs in the same NMR region as do the protons of coordinated cyclopentadienyl. Both ligands display the symmetrical sandwichlike bond with their metals. Today, however, it is clear that the complexes differ significantly in type, the difference being associated first of all with the fact that π -allyl complexes are much more efficient than π -cyclopentadienyls at transforming to σ -allyl or π -olefin compounds. This may be due to the difference between the delocalization energies, 2.472 and 0.828 eV for cyclopentadienyl and allyl anions, respectively (426).

We studied allyliron tricarbonyl halides obtained earlier by Plowman and Stone (427) and by others (428, 429). The compounds were taken because (1) they are complexes of iron, the metal whose cyclopentadienyl derivatives were under thorough study in our laboratories, and (2) octahedral π -allyl complexes were scarcely known at that time, so it was challenging to compare them with the square-planar π -allyl complexes which were extensively studied in the USSR as well as elsewhere.

Struchkov and other colleagues (430–432) found that allyliron tricarbonyl halides and their monophosphine derivatives possessed structure (XIX), where X is halogen. The allyl group is symmetrical within the X-ray accuracy. In solutions, however, the rotational structure (XX) was observed (PMR) together with (XIX).

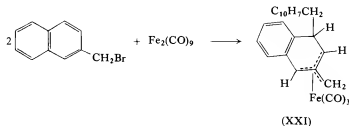


The ratio of (XIX) to (XX) decreased regularly in the series π - $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}$, π - $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{Br}$, π - $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{Cl}$. This might be governed by the overall energies of the isomers, the relative energies depending on the relation of the donor–acceptor interactions which characterize the allyl–metal and metal–halogen bonds, rather than by spatial requirements of the covalent group X. We synthesized the bis(π -allyl) complex $(\text{C}_3\text{H}_5)_2\text{Fe}(\text{CO})_2$ (433), which was dynamically equilibrated in solution, the MX part of two AM_2X_2 spectra being averaged at room temperature. The activation energy was found to be close to 5 kcal/mole. The process is hard to rationalize thus far. It may comprise π -rotation or the averaging of asymmetric π -allyl groups. Complexes substituted at the allyl group, and the nitrate ($\text{X} = \text{NO}_3$), which is the most polar compound of this type, display just one of the rotational forms (434).

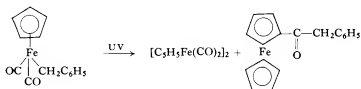
The reactions of allyliron tricarbonyl halides with donor molecules were studied. Triphenylphosphine substituted only one carbonyl, that trans-oriented with respect to the halogen of the form (XIX) (432). The phosphine derivatives of (XX) were not isolated as pure compounds. The complexes were decomposed entirely by dimethyl sulfoxide, giving $[(\text{CH}_3)_2\text{SO}]_5\text{FeX}_2$ (435). Thermal decomposition of $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{X}$ depended on the medium and gave either diallyl, or diallyl ketone, together with propene, allyl ether, $\text{Fe}(\text{CO})_5$, and FeX_2 (436).

Today, we are studying whether iron can coordinate to aromatics and give, among other things, π -benzyl derivatives. The π -benzyl ligand is a modification of the π -allyl one. So far, however, the coordination has been shown to be not too favorable. Actually ArCH_2X (X is Cl, or Br) reacts with di-iron nonacarbonyl to produce, as a rule (437), $\text{ArCH}_2\text{CH}_2\text{Ar}$ or

$\text{ArCH}_2\text{COCH}_2\text{Ar}$ with the unstable σ -derivative being possible intermediates. Naphthalene, a more flexible system, reacts in a rather surprising manner so that β -methylnaphthalene yields the trimethylenemethane complex (XXI) (438).



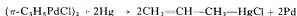
Photochemical rearrangement of a σ -compound, $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{-CH}_2\text{C}_6\text{H}_5$, to the π -form was also unsuccessful, though analogous transformations were reported by King for molybdenum and tungsten. σ -Benzyl- π -cyclopentadienylirondicarbonyl when irradiated in hexane gave cyclopentadienylirondicarbonyl dimer together with small amounts of phenylacetylferrocene (439).



In collaboration with Gubin and Rubezhov (440) we compared the π -allyl and π -cyclopentadienyl ligands bonded to the same atom, palladium. In all reactions of π -cyclopentadienyl- π -allylpalladium the π -allyl was bonded to the metal more strongly than the π -cyclopentadienyl. Reactions with HCl , HgCl_2 , or FeCl_2 gave $(\text{C}_5\text{H}_5\text{PdCl})_2$ and cyclopentadiene, cyclopentadienylmercury chloride, and ferrocene, respectively. The reaction with $\text{C}_4\text{H}_9\text{Li}$ also abstracted the cyclopentadienyl group with the formation of $\text{C}_{10}\text{H}_{10}\text{Li}_2$.

The compound $(\text{C}_5\text{H}_5\text{PdCl})_2$, though very stable, proved able to transfer its π -allyl groups to iron or mercury. The first reaction was the interaction of $(\text{C}_5\text{H}_5\text{PdCl})_2$ with $\text{Fe}_2(\text{CO})_9$, which gave $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_3\text{Cl}$ (441). The second reaction, the transfer to a less noble metal (from palladium to

mercury), resembles the reaction discovered by Kocheshkov and the author, the transfer of aryl from Ar_2Hg to tin:



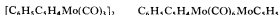
The π -bonded ligand becomes σ -bonded. The reaction was carried out with a number of substituted allyls and the mechanism was studied (442, 443).

XIX

σ -ARYLATED COMPLEXES

An organometallic chemist will inevitably be interested in σ -alkyl and -aryl complexes of transition metals. Initially thought to be nonexistent, these compounds were eventually prepared in large variety, especially as the complexed derivatives. A group of my co-workers (Makarova, Chapovskii, N. Ustynyuk, and others) were initially interested in whether the diazo method could be applied to the synthesis of the ArMLn ($\text{Ln} = \text{CO}$ or $\pi\text{-C}_5\text{H}_5$). However, $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2^-$ arylated by ArN_2BF_4 gave only $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ and traces of $\text{ArFe}(\text{CO})_2\text{C}_5\text{H}_5$. Other, less oxidizing, onium cations proved more effective. Actually, $(\text{C}_6\text{H}_5)_2\text{IBF}_4$ gave about 20%, while $(\text{C}_6\text{H}_5)\text{SBF}_4$ gave 40%, of the desired σ -phenyl- π -cyclopentadienyliron dicarbonyl (444).

Similarly, we arylated $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3$ by diphenyliodonium tetrafluoroborate and obtained $\pi\text{-C}_5\text{H}_5\text{W}(\text{C}_6\text{H}_5)(\text{CO})_3$ (446) and small amounts of $[\text{C}_6\text{H}_5\text{C}_5\text{H}_4\text{W}(\text{CO})_3]_2$. The first compound, when heated to 100°C , underwent the rearrangement of its phenyl from the metal to the cyclopentadienyl (ricochet substitution) and produced $[\text{C}_6\text{H}_5\text{C}_5\text{H}_4\text{W}(\text{CO})_3]_2$ (447). The phenylation of $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3$ by diphenyliodonium tetrafluoroborate did not allow us to isolate a possible phenylated intermediate and only the ricochet phenylation products were identified, viz.,



The simultaneous formation of $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ indicated the presence of the intermediate free radicals $\text{C}_6\text{H}_5\text{C}_5\text{H}_4\text{Mo}(\text{CO})_3$ and $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3$.

Cyclopentadienyl tricarbonyl tungsten anion arylated by benzenediazonium tetrafluoroborate gave $\pi\text{-C}_5\text{H}_5\text{W}(\text{C}_6\text{H}_5)(\text{CO})_3$ in a yield as low as 3%. The main product was identified as $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2\text{N}=\text{NC}_6\text{H}_5$,

analogous to the Mo compound obtained earlier by King and his co-workers (448).

The carbonyl groups of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Ar}$ could be substituted by one or two triphenylphosphite ligands under the action of light. The compound $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OPh})_3]_2\text{C}_6\text{H}_5$, when heated did not transfer its phenyl group to the ring and gave biphenyl and $\{\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OPh})_3]_2\}_2$ (449).

This dimer when treated with iodine produced $\pi\text{-C}_5\text{H}_5\text{Fe}[\text{P}(\text{OPh})_3]_2\text{I}$, whose structure was proved by the formation of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ under the action of CO. Apart from the latter carbonyl, a deeper colored compound was formed whose properties and elemental analysis were close to those of the carbonyl. The compound was thought to be the isomer of the carbonyl, but the X-ray analysis showed that the carbon of one of the phenyls was bonded in a striking manner to a carbon of the cyclopentadienyl (445).

We studied the polarography of the compounds $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{PPh}_3)\text{-C}_6\text{H}_4\text{R-}p$ (Series 1) and, on the other hand, $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$ (Series 2). The half-wave reduction potentials obtained for Series 1 compounds correlated well with the Hammett σ_p^0 parameters. The potentials obtained for Series 2 correlated well with the IR frequencies (antisymmetric and symmetric) of the CO groups. The frequencies, in turn, correlated with the σ_i parameters best of all (450).

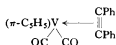
Hence, a substituent bonded to iron transfers its effect to the other ligand according to an inductive mechanism, as was found earlier by Gubin and the author for the related compounds.

XX

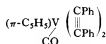
π -ACETYLENE COMPLEXES OF TRANSITION METALS

The reader may remember that the π -complex structure for the adducts formed from acetylene and mercury dichloride, or of related complexes of non-transitional-metal halides, was disproved by our stereochemical investigations. The true π -complexes, however, were also obtained by us from tolan and the derivatives of such transition metals as V, Nb, and Ta (451-455). π -Cyclopentadienylniobium tetracarbonyl reacted with tolan according to the scheme shown on page 57.

The compound $(\pi\text{-C}_5\text{H}_5)\text{Ta}(\text{CO})_4$ gave another such series of tolan complexes, which were transformed in a quite similar fashion. The photochemical reaction of $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ with tolan produced



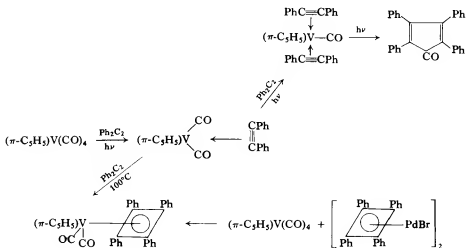
and



The first complex, when heated with tolan in the absence of light, produced $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\pi\text{-Ph}_4\text{C}_4)$, which was obtained via an independent route from



and $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$. The transformations of all our vanadium complexes may be described by the following pattern:



We found also that $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3\text{PPh}_3$ as well as its niobium analog, when irradiated, underwent substitution of one PPh_3 and one CO by tolan. Hence, niobium (and tantalum) complexes of the type are able to attach a third molecule of tolan and transform this to hexaphenylbenzene, unlike the vanadium analog, which transforms just two tolans to tetraphenylcyclobutadiene or, if irradiated, combines them with carbon monoxide and produces tetraphenylcyclone.

XXI. CONCLUSION

My scientific research started at the Organic Chemistry Department of Moscow University, where in 1934 I organized and directed the work of the Organometallic Laboratory. In 1935 I was asked to set up an Organometallic Laboratory in the Institute of Organic Chemistry of the USSR Academy of Sciences, and henceforth investigations were carried out in both laboratories. Organometallic chemistry is inseparable from organic chemistry. Moreover, it seems rather arbitrary to state that boron or silicon chemistry does, while phosphorus (unlike arsenic, antimony, etc.) chemistry does not, belong to the organometallic domain. In the Organometallic Laboratory of the USSR Academy of Sciences, we disregard this artificial boundary and investigate organophosphorus, organofluorine, and organopolychlorine chemistry. These researches could not be mentioned in this chapter but they led to the formation of a number of filial organo-element laboratories in the Institute of Organic Chemistry (in about 1950). Consequently, in 1954, I, in my capacity of President of the USSR Academy of Sciences (1951–1961), could state and resolve the problem of the formation of the Institute of Organo-Element Compounds. The Institute deals with the organometallic chemistry of the main group metals and also the chemistry of the metalloids (B, Si, P), as well as organohalogen chemistry and organometallic chemistry of transition elements.

I am confident that the work of the Institute of Organo-Element Chemistry reflects the vivid character of modern chemical science, and the need for creating an organic chemistry for each element of the Periodic System. In this manner, organometallic chemistry provides a bridge between organic and inorganic. As organo-element chemistry advances, the bridge is transformed into an isthmus which will unite both continents of chemistry.

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* The page number, e.g., W. p. 736, after a journal reference refers to the page in the Volume: A. N. Nesmeyanov, "Selected Works in Organic Chemistry," Pergamon, Oxford, 1963.

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Electronic Effects in Metallocenes and Certain Related Systems

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I. Introduction	79
II. Homoannular Electronic Effects	80
A. Relative Site Reactivities	80
B. Spectroscopy	82
III. Substituent Effects on the Ring-Metal Bond	91
A. Ligand-Exchange Studies	91
B. Mass Spectroscopy	95
IV. Substituent Effects on the Heteroatom. Oxidation-Reduction Potentials	98
V. Interannular Electronic Effects	101
A. Relative Site Reactivities	101
B. Spectroscopy	102
C. Dissociation Constants of Ferrocenoid Acids	106
VI. The Electronic Influence of Ferrocenyl and Related Groups as Substituents	107
VII. Conclusion	110
References	111

I

INTRODUCTION

Electronic effects of substituents can affect organic molecules in diverse ways. Usually, loci near the substituent are most influenced, but often electron density is altered several bonds removed from the substituent. Aromatic organometallic π -complexes provide fascinating systems for the study of substituent effects, for the three-dimensional nature of these complexes adds interesting complexities to the analysis of the distribution of electron density in such molecules. This chapter is intended to summarize homoannular, interannular, and metal-ring substituent effects in metallocene and similar systems with the idea of spurring additional research in the area.

One fact emerges quite clearly from this review: electronic effects in metallocene systems do not parallel systematically such effects in aromatic

hydrocarbons. It also seems probable that electronic effects in the various metallocene systems do not parallel one another. The exact contribution of the metal atom to the overall electron density distribution in such molecules cannot at present be reliably determined.

II

HOMOANNULAR ELECTRONIC EFFECTS

Since all aromatic organometallic π -complex systems possess several possible sites for which substituent effects could be analyzed, it seems best that the various sites be studied independently of one another. One particular site, the substituted ring, has been shown to be amenable to such analysis. The electronic effects on the substituted ring in ferrocenes, i.e., homoannular electronic effects, have recently been the subject of an extensive review (75). For this reason discussion of ferrocene systems in this section will be abbreviated and attention will be focused upon recent advances in related metallocene and other aromatic organometallic systems.

Two distinct approaches to the elucidation of homoannular electronic effects within the transition metal-complexed aromatic ring have been utilized: (1) relative site reactivities and (2) NMR spectroscopy. Because of the relative availability of many ferrocene derivatives considerable attention has been devoted to this system. In several instances results for the ferrocene system have provided a basis for the analysis of electronic effects in related organometallic π -complexes.

A. Relative Site Reactivities

1. Isotopic Exchange

The study of relative site reactivities for aromatic electrophilic substitution reactions has provided useful information for assessing homoannular electronic effects within the ferrocene system. Ferrocenes of the type (I)



which contain strongly electron-donating groups show enhanced reactivity toward deuterium exchange, whereas ferrocenes containing strongly electron-withdrawing groups show decreased overall reactivity of the ferrocene nucleus (36, 37, 48, 49). Classification of substituents as activators or deactivators was found to parallel that of the substituents when on the benzene system. However, the relative reactivity of the substituted ferrocene nucleus did not provide any information regarding relative *site* reactivities within the substituted ferrocene system.

2. Electrophilic Substitution

The product distribution from various electrophilic substitution reactions of monosubstituted ferrocenes has been studied by a number of workers (75). Differing reactivities for the 2,5- and the 3,4-position were found in all cases, but often electronic effects could not be separated from steric and other factors. A complete tabulation of the site reactivities of a group of ferrocenes is given in Table I (34). This table is limited to those ferrocenes which contain activating or only slightly deactivating groups, since strongly deactivating groups force substitution to take place in the unsubstituted ring only (26), thus precluding any homoannular electronic effect assessment. One apparent discrepancy merits special attention at this point. Both the alkyl and alkoxy or thioalkoxy groups are noted to have similar electron-donating properties. Whereas the alkyl group on ferrocene generated enhanced reactivity at the 3-position (4, 60), the alkoxy and thioalkoxy ferrocenes exhibited enhanced reactivity at the 2-position (34). This apparent reversal of site reactivities of the alkoxy derivative has been explained by (1) a resonance contribution of the form (II) or by (2) an ortho



effect which involved initial attack of the electrophile at the heteroatom and then rearrangement to a σ transition state at the ring position closest to the heteroatom.

TABLE I
RELATIVE SITE REACTIVITIES OF MONOSUBSTITUTED AND
1,1'-DISUBSTITUTED FERROCENES TOWARDS ELECTROPHILES^a

R ¹	R ²	Relative site reactivities		1'	Type of reaction ^b
		2	3		
Me	H	0.75	1	0.625	A
Me	H	0.58	1	0.15	B
Me	Me	0.44	1	—	A
Me	Me	0.61	1	—	B
Me	Me	0.44	1	—	C
Et	H	0.33	1	0.24	A
Et	H	0.45	1	0.53	A
Et	Et	0.39	1	—	A
Et	Et	0.44	1	—	A
Et	Et	0.48	1	—	D
iso-Pr	H	0.25	1	0.42	A
iso-Pr	iso-Pr	0.23	1	—	A
tert-Bu	H	0.08	1	0.30	A
Ph	H	1.64	1	2.13	A
Ph	Ph	1.65	1	—	A
<i>p</i> -MeOPh	H	1.94	1	1.68	A
<i>p</i> -MeOPh	<i>p</i> -MeOPh	1.95	1	—	A
<i>p</i> -BrPh	<i>p</i> -BrPh	1.11	1	—	A
MeO	H	1.6	1	0.43	B
MeO	MeO	1.8	1	—	B
MeS	H	1.45	1	0.6	B
MeS	MeS	1.9	1	—	B

^a Knox *et al.* (34).

^b A = Acetylation; B = aminomethylation; C = isobutyrylation; D = succinylation.

B. Spectroscopy

1. NMR

a. *Ferrocenes*. The limited information available and the presently conflicting relative site reactivity data precluded any definitive conclusions concerning the relative ordering of electron density in monosubstituted ferrocenes. An alternative approach was required. NMR spectroscopy has been applied in the correlation of electron density with the chemical shift values of the ortho, meta, and para protons of monosubstituted benzenes

(83). Since monosubstituted ferrocenes contain only two distinct homoannular positions, the ferrocenes system would appear to be an easier one than benzene for analysis of PMR effects.

The PMR data compiled for the monosubstituted ferrocene system have recently been reviewed and assessed for their relative importance with respect to the electronic effects in that system (75, 76). Monosubstituted ferrocenes exhibit three distinct signals in their PMR spectra, namely, those which arise from the unsubstituted ring protons (H'_1), those which arise from the 2- and the 5-position protons ($H_{2,5}$), and those which arise from the 3- and 4-position protons ($H_{3,4}$). The H'_1 protons in these compounds exhibited a five-proton singlet while the $H_{2,5}$ and $H_{3,4}$ protons were in most cases resolvable into two-proton apparent triplets. These are termed apparent triplets because of the near equivalence of the adjacent and cross-ring coupling constants (39). The relative extent of shielding or deshielding of the $H_{2,5}$ and the $H_{3,4}$ protons (since we are only concerned with homoannular effects) will depend entirely upon the electronic nature of the substituent. However, electronic perturbation of a five-membered aromatic ring offers new problems in the interpretation of the actual experimental data.

Table II lists the chemical shift values for a representative group of substituted ferrocenes. Upon examination of this table it becomes evident that categorization of these substituents according to their relative shielding/deshielding effects is possible. These substituents can be divided into four main classes.

- (1) Substituents which *deshield* both the $H_{2,5}$ and $H_{3,4}$ protons.
- (2) Substituents which *shield* both the $H_{2,5}$ and $H_{3,4}$ protons.
- (3) Substituents which *shield* the $H_{3,4}$ protons and *deshield* the $H_{2,5}$ protons.
- (4) Substituents which *shield* the $H_{2,5}$ protons but *deshield* the $H_{3,4}$ protons.

In each class, unequivocal assignments have been made via specific deuterium labeling techniques (65, 77, 78).

Differentiation of the $H_{2,5}$ and $H_{3,4}$ chemical shift values was possible for all monosubstituted ferrocenes with the exception of the alkylferrocenes, which required use of a Varian 220 MHz spectrometer for resolution (77). The results are tabulated in Table III. It is particularly interesting that the

TABLE II
PMR CHEMICAL SHIFT VALUES (ppm) OF MONOSUBSTITUTED
FERROCENES $[XC_5H_4FeC_5H_5]$ FROM TMS^{a, b}

Class	X	δ (2, 5)	δ (3, 4)	δ (1')
Ferrocene	H	4.041	4.041	4.041
	CHO ^{c, d}	4.697	4.468	4.198
	CN ^c	4.596	4.296	4.296
	COPh	4.801	4.428	4.112
	CO ₂ Et	4.699	4.263	4.113
	1 { COCH ₃	4.659	4.359	4.120
	NO ₂	5.158	4.386	4.290
	SO ₂ NMe ₂ ^{c, e}	4.484	4.271	4.351
	CON ₃ ^c	4.735	4.400	4.185
	CONHPh ^c	4.671	4.298	4.184
	2 { CH ₃ ^f	3.919	3.919	3.965
	CH ₂ CH ₃ ^f	3.933	3.933	3.979
	CH(CH ₃) ₂	3.934	3.934	3.997
	C(CH ₃) ₃ ^f	3.933	3.933	4.030
	NH ₂ ^{c, g}	3.833	3.698	3.954
	OCH ₃ ^{c, g}	3.960	3.692	4.078
	3 { I ^h	4.326	4.057	4.106
	Cl ^c	4.298	3.950	4.146
	Br ^c	4.324	3.998	4.139
	OAc ^c	4.350	3.818	4.103
	NHCO ₂ CH ₂ Ph ^c	4.356	3.840	4.028
4	Si(CH ₃) ₃ ^{c, i, j}	3.980	4.213	4.019

^a This list is significantly expanded from that published in our recent review (75).

^b All spectra were obtained on a Varian HA-100 Spectrometer for samples of 3 mole % in CCl₄ with TMS internal standard at 34°C. Estimated error in δ is 0.004 ppm.

^c Assignments based on spectrum of the corresponding 2-deutero compound.

^d Rausch and Siegel (65).

^e W. Achermann and D. W. Slocum, unpublished results.

^f The 2,5- and 3,4-proton signals for these molecules were resolved on a 220 MHz instrument (cf. Table III).

^g These assignments for H_{2, 5} and H_{3, 4} have been reversed from those originally published by Dvoryantseva *et al.* (16); cf. also Slocum *et al.* (73).

^h M. D. Rausch, private communication.

ⁱ Hexane internal standard.

^j Slocum and Ernst (74).

$H_{3,4}$ protons are more highly shielded than the $H_{2,5}$ protons and that the efficiency of this differential shielding passes through a minimum in the progression from the methyl to the *tert*-butyl substituent. This shielding parallels the hyperconjugative (resonance) contribution (both C—H and C—C) to the $H_{3,4}$ shift in each of the members of this series.

This leads to a most salient point. Those ferrocenes within classes 2 and 3 all exhibited an unusual phenomenon, namely, shielding was chiefly manifested at the 3,4-position protons. Each substituent within these two

TABLE III
SHIELDING VALUES (ppm) OF RING PROTONS OF
ALKYLFERROCENES FROM FERROCENE^{a,b}

Alkyl group	H_1	$H_{2,5}$	$H_{3,4}$
CH_3^c	+0.077	+0.109	+0.146
$CH_2CH_3^c$	+0.064	+0.105	+0.114
$CH(CH_3)_2$	+0.050	+0.114	+0.114
$C(CH_3)_3$	+0.023	+0.096	+0.132

^a Slocum *et al.* (77).

^b Spectra obtained for 3 mole % solution in CCl_4 at 20°C with 2% TMS internal standard on a 220 MHz Varian Spectrometer.

^c Assignments based on spectrum of corresponding 2-deutero compound.

classes is classically an electron-donating substituent by resonance. Correlating these two factors leads to the conclusion that resonance effects appear to be directed chiefly to the 3- and 4-positions. Inductive effects of course are chiefly reflected at the 2,5-position protons. Even the presently accepted electron-withdrawing character of the trimethylsilyl substituent (class 4) was consistent with a resonance effect being manifested at the 3- and 4-positions (82). Electron withdrawal via the *d* orbitals on silicon should deshield $H_{3,4}$, a fact which has been verified by the PMR spectrum of 2-D-trimethylsilylferrocene (74). The large anisotropic deshielding effect of the class 1 substituents precludes the same kind of assessment of the relative contribution of resonance and inductive effects in these compounds.

b. *Arenecyclopentadienyl Iron Complexes.* The PMR spectra of a series of monosubstituted derivatives of π -complexes other than ferrocene have been

analyzed, but to date no specifically deuterated derivatives have been prepared in order that unequivocal assignments to the various absorptions may be made. One such complex is the benzenecyclopentadienyliron cation, which Nesmeyanov and co-workers have studied extensively over the past few years. Analysis of the PMR spectra of two series of monosubstituted derivatives, one of each ring, have now been published (50). Chemical shift data for the complexes containing substituted benzene ligands (III)

TABLE IV
PMR CHEMICAL SHIFT (ppm) AND SHIELDING (ppm) VALUES OF
[XC₆H₅FeC₅H₅]⁺PF₆^{-a, b}

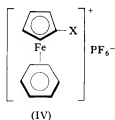
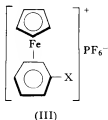
X	δ (C ₅ H ₅)	Δδ (C ₅ H ₅)	δ (C ₆ H ₅ X) ^c
NH ₂	4.95	+0.24	6.01
CH ₃	5.13	+0.06	6.35
C ₂ H ₅	5.15	+0.04	6.38
OCH ₃	5.15	+0.04	6.33
NHCOCH ₃	5.15	+0.04	6.58
Cl	5.31	-0.12	6.64
F	5.32	-0.13	6.63
CN	5.47	-0.28	6.86
H	5.19	0.00	6.44
CO ₂ H	5.27	-0.08	6.81
CO ₂ Et	5.24	-0.05	6.82
CONH ₂	5.22	-0.03	6.74
OC ₆ H ₅	5.23	-0.04	6.35

^a Nesmeyanov *et al.* (50).

^b Spectra were obtained for samples at 0.2 M concentration in deuterioacetone with hexamethyldisiloxane.

^c Approximate center of multiplets.

and substituted cyclopentadienyl ligands (IV) are summarized in Tables IV and V, respectively. Since differences in the chemical shifts of the



various benzene ring protons were not obtained, homoannular electronic effects for complexes of the type shown in structure (III) cannot be analyzed at present, although the relative shielding/deshielding of the benzene protons as a group seems to parallel that expected from the known electronic properties of each substituent. However the complexes of general structure (IV) exhibited PMR spectra which allowed resolution of the $H_{2,5}$ and $H_{3,4}$ proton resonances on the substituted cyclopentadienyl ring. The authors did not attempt assignments for the $-NHCOCH_3$, $-SC_6H_5$, or the

TABLE V
PMR CHEMICAL SHIFT (ppm) AND SHIELDING (ppm) VALUES OF
[$XC_5H_4FeC_6H_5$] $^+PF_6^-^{a,b}$

X	δ (C_6H_6)	$\Delta\delta$ (C_6H_6)	2-Position	3-Position
C_2H_5	6.39	+0.05	5.12	5.12
OCH_3	6.45	-0.01	4.94	5.14
H	6.44	0.00	5.19	5.19
Cl	6.51	-0.07	5.53	5.21
NH_2	6.16	+0.28	4.78	4.84
$COCH_3$	6.52	-0.08	5.70	5.46
CO_2H	6.55	-0.11	5.65	5.40
$NHCOCH_3$	6.36	-0.09	5.01 or 5.53	5.53 or 5.01
SC_6H_5	6.41	+0.03	5.23 or 5.21	5.21 or 5.23
$N(CH_3)_2$	6.33	+0.11	4.95 or 4.75	4.75 or 4.95
OC_2H_5	6.43	+0.01	4.94	5.14

^a Nesmeyanov *et al.* (50).

^b Spectra were obtained for samples at 0.2 M concentration in deuterioacetone with hexamethyldisiloxane as internal reference.

$-N(CH_3)_2$ substituents; assignments for the remaining groups were presumably based on the assignments to the analogous ferrocene derivatives published by Gubin and co-workers (16). It was reported that those complexes containing electron donor groups exhibited their greatest shielding at the 2,5-position. The assignments for the compounds possessing withdrawing groups paralleled those of their ferrocene analogs (Table II) whereas the assignments for compounds possessing electron donor groups, although in accord with the earlier tentative ferrocene assignments published by Gubin *et al.* (16), were at variance with the presently revised assignments (Table II) (77, 78). Since information concerning the reliability of equating

the relative chemical shifts in these complexes with those of ferrocene is totally lacking, assignments in these complexes must be considered as tentative.

c. *Cobalticinium Salts*. A similar organometallic cation system containing cobalt has been investigated. Rausch and Sheats have recently described the preparation and PMR spectra of a series of substituted cobalticinium hexafluorophosphates (71). Chemical shift data for these salts are given in Table VI. Those salts containing electron donor groups ($-\text{CH}_3$ and $-\text{NH}_2$) exhibited shielding of all ring protons in the spectrum (relative to the

TABLE VI
CHEMICAL SHIFTS (ppm) OF THE VARIOUS RING PROTONS
OF SUBSTITUTED COBALTICINIUM SALTS^a

Substituent (R)	Cobalticinium salt		
	H _{ring}	H _{2,5}	H _{3,4}
H ^b	6.25	—	—
NO ₂ ^b	6.23	6.80	6.17
CO ₂ H ^b	6.04	6.33	6.09
COCl ^d	6.00	6.41	6.10
CO ₂ CH ₃ ^c	6.00	6.33	6.07
CH ₃ ^c	6.13	6.10	6.10
NH ₂ ^b	5.53	5.50	5.38

^a Sheats and Rausch (71).

^b Solvent acetone.

^c Solvent acetone-*d*₆.

^d Solvent CF₃CO₂H.

unsubstituted salt) with the same relative assignment to H_{2,5} and H_{3,4} as in the case of aminoferrocene having been made (cf. Table II). Those substituents which are usually considered strongly deshielding effectively deshield *only* the 2,5-position protons, which is an interesting variation on the deshielding of both the 2,5- and 3,4-position protons in similarly substituted ferrocenes (Table II). Evidently withdrawal of electron density from the cobalticinium cation is not as effective due to the high oxidation state of the cobalt atom (+3). The large anisotropy of the carbonyl group must account for the deshielding of the 2,5-position protons. Interestingly, chemical shift data for this salt system were not analogous to those for arene-cyclopentadienyl iron complexes, in which effective deshielding was ex-

perienced at all positions relative to the unsubstituted parent complex (Table V).

d. *Cymantrenes*. With the recent technological interest in cymantrene (cyclopentadienylmanganese tricarbonyl) review of structural studies of this molecule seems most timely. Spectral data are available which allow partial analysis of this compound (72). The chemical shifts of the ring

TABLE VII
CHEMICAL SHIFTS OF THE RING PROTONS
OF MONOSUBSTITUTED CYMANTRENES^{a, b}

Substituents	τ Values of ring protons	
	H _{2, 5}	H _{3, 4}
CHO	4.22	4.75
COCH ₃	4.26	4.84
CONH ₂	4.36	4.99
CO ₂ H	4.42	4.89
CCH ₃ =NOH	4.70	5.09
P(O)OH	4.48	4.76
SO ₂ H	4.55	4.95
H	5.04	5.04
CH ₃	5.21	5.21
CH(CH ₃)NH ₃ ⁺ Cl ⁻	5.01	4.62
HgCl	5.06	4.98
NHCO ₂ CH ₂ Ph	4.95	5.18
NHCOCH ₃	4.86	5.22

^a Shen *et al.* (72).

^b Solvent DMSO-*d*₆ with tetramethylsilane as internal reference.

protons of a representative list of substituted cymantrenes are given in Table VII. Assignments of these chemical shifts were made on the basis of the related shifts in their respective benzene and ferrocene analogs. Deshielding is experienced by all protons in those cymantrenes which possess strongly electron-withdrawing groups. The large anisotropic deshielding effect of the carbonyl group presumably is the main effect accounting for the deshielding observed. For those cymantrenes which contain the chloromercuri, urethane, and acetylated amine groups, strongest shielding is experienced by the 3,4-position protons. These assignments

parallel those in the ferrocene system. The limited number of donating groups present in this study precluded further assessment of correlations here.

All four organometallic cyclopentadienyl systems discussed heretofore have had their homoannular electronic effects examined by PMR spectroscopy. Of the four, only the cobalticinium salts exhibited shielding for the 3,4-position protons relative to the unsubstituted complex when electron-withdrawing groups were present; in the other three complexes, both the 2,5- and 3,4-position protons were deshielded. Although the electronic properties of the cobalticinium salt as a substituent have not been determined, it is likely that its electron-withdrawing power would exceed that of an acyl-type substituent. If this is the case, possible shielding at $H_{3,4}$ may result since the normal electron-attracting groups may now donate with respect to the cobalticinium nucleus. The anisotropic effect of the carbonyl substituents would not be influenced by this; thus the normal deshielding of the 2,5-position protons would be observed. For strongly electron-donating substituents, shielding is found for every case.

One final point must be made. We have demonstrated in these laboratories that assignments of the chemical shift values of the ring protons for substituted ferrocenes based on analogy to the corresponding benzene compounds leads to incorrect assignments. It is quite possible that analogy will not suffice for assignment of chemical shifts within diverse cyclopentadienyl systems. Thus the assignments in the substituted arenecyclopentadienyl iron cation, the substituted cobalticinium salt system, and the substituted cymantrene system must be considered tentative until specific deuterium-labeled derivatives in each system can be prepared.

2. *UV Spectra*

UV data collected from substituted ferrocene systems have been summarized by Rosenblum (68) and some analysis of the electronic transitions involved has been provided. Until recently, little use had been made of the extensive tabulation of UV data of various substituted ferrocenes found in the literature. Several Russian workers have now attempted a qualitative correlation of the absorption bands of a series of mono- (20) and 1,1'-disubstituted (19) ferrocenes with the nature of the substituent. For each of the four different absorption bands observed in the spectra of these substituted ferrocenes, both bathochromic and hypsochromic shifts were exhibited for those ferrocenes containing electron-donating or -withdrawing

groups, but not necessarily respectively. The lack of uniformity in the nature of the shifts within a particular grouping of substituents, either electron donating or withdrawing, made electronic effect assessments impossible. However, the authors did comment upon the similarity of the influence of the substituents on the shift of the $260\text{ m}\mu$ band in the ferrocenes and the $200\text{ m}\mu$ band found in the spectra of substituted benzenes.

More recently, UV data for a related system, substituted cobalticinium salts (71) have been tabulated. A similarity in the positions of the absorption bands in this system and the analogous substituted ferrocenes was observed. A decrease in the absorbance of the band at $260\text{--}275\text{ m}\mu$ with both donating and withdrawing groups was the only electronic effect of note.

III

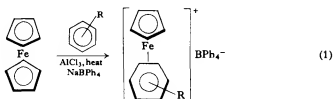
SUBSTITUENT EFFECTS ON THE RING-METAL BOND

In the preceding section it was observed that the nature of the substituent has a substantial effect upon the chemical and physical properties of the ring to which it is bonded. This effect, whether it be transmitted by resonance or induction, should exert some influence upon the bonding between the ring and the metal atom. It is our aim in this section to discuss the effect of substituents on the ring-metal bond in various organometallic π -complexes. Two methods have been utilized in such studies, namely, (1) ligand-exchange reactions and (2) mass spectrometry, a more physical probe. In the ensuing discussion each technique will be introduced separately and a comparison of the conclusions from each study will be presented.

A. Ligand-Exchange Studies

Although numerous π -bonded organometallic complexes are known today, ligand-exchange studies have been performed on few systems other than the metallocenes, and of these only ferrocene has been studied extensively. Despite the enhanced stability of the ferrocene system, its cyclopentadienyl rings have recently been shown to possess a significant degree of mobility under certain conditions. These rings can be displaced quite readily with other aromatic ligands upon heating with AlCl_3 . For example, Nesmeyanov *et al.* (53) have shown that benzenecyclopentadienyl iron complexes can be prepared by heating ferrocene in a benzene/ AlCl_3 solution, as shown in Eq (1). Similar treatment of the appropriate aromatic

compound afforded isolable complexes of mesitylene-, naphthalene-, and tetralincyclopentadienyliron tetraphenylborates.



The first indication of an electronic effect in the ring migration studies was demonstrated when 1,1'-diethylferrocene was observed to undergo ligand exchange with mesitylene much more readily than did ferrocene

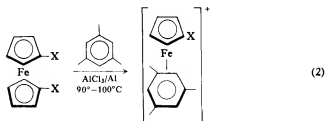
TABLE VIII

YIELD OF MESITYLENECYCLOPENTADIENYLIRON DERIVATIVE FROM THE REACTION OF MESITYLENE AND SUBSTITUTED FERROCENE^a

Substituent X in Eq. (2)	% Yield mesitylene complex
C ₂ H ₅	32
H	20
OCOCH ₃	4

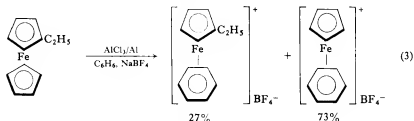
^a Nesmeyanov *et al.* (56).

itself (55). A more comprehensive study of various substituted ferrocenes is summarized in Table VIII for the reaction shown in Eq. (2) (56). Electron-



withdrawing groups on the ferrocene rings facilitate ligand exchange whereas electron-withdrawing groups impede such exchange (56). Also, in

ethylferrocene the alkyl group weakens the alkylated ring-iron bond compared to the unsubstituted ring-iron bond [Eq. (3)].



However, when acetylferrocene was subjected to similar conditions using mesitylene, the product mixture contained a preponderance of the acetylcyclopentadienylmesitylene iron complex, suggesting that electron-withdrawing groups strengthen the acetylated ring-metal bond more than the unsubstituted ring-metal bond.

Further studies have shown that the extent of ligand exchange within the ferrocene system varies with the nature of the substituting ligand. Nesmeyanov and co-workers (54) have performed exchange reactions on ferrocene with various substituted benzenes. The data suggest that those benzenes which undergo Friedel-Crafts reactions more readily likewise exhibit enhanced ligand-exchange reactivity, i.e., electron-donating groups on the benzene ring facilitate exchange whereas electron-withdrawing groups impede exchange.

The lability of the cyclopentadienyl rings within the ferrocene system is also demonstrated by several disproportionation and synproportionation (disproportionation of a mixture of two different ferrocenes) studies of the alkylferrocenes. For example, *n*-propylferrocene has been shown to disproportionate into ferrocene and 1,1'-di-*n*-propylferrocene upon heating with AlCl_3 in dichloromethane (8). Although detailed mechanistic studies of these reactions are lacking, the data suggest that in a solution containing AlCl_3 a substituted ferrocene molecule $[\text{C}_5\text{H}_5\text{FeC}_3\text{H}_4\text{X}]$ may exist as a positive and a negative fragment, either $[\text{C}_5\text{H}_5\text{Fe}]^+$ and $[\text{C}_5\text{H}_4\text{X}]^-$ or $[\text{XC}_3\text{H}_4\text{Fe}]^+$ and $[\text{C}_5\text{H}_5]^-$. The anion fragments may be stabilized by complexation with AlCl_3 . Proof of the ring-metal scission was obtained by the disproportionation of 1,2,1'-triethylferrocene which afforded a mixture of 1,1'-diethyl-, 1,2,1'-triethyl-, and 1,2,1',2'-tetraethylferrocene. In addition, a trace amount of ethylferrocene was formed, presumably by a dealkylation reaction. If these reactions were occurring by ring-alkyl group

scission, other isomeric ethylferrocenes should have been found. However, none were detected during the detailed examination of product mixtures from these reactions.

Highly ethylated ferrocenes were subjected to similar conditions and a correlation between the number of ethyl groups on a ferrocene ring and the migratory ability of the ring was attempted (9). Although 1,2,3- and 1,2,4-triethylferrocene were observed to disproportionate, 1,1',2,3'-tetraethyl-, nonaethyl-, and decaethylferrocene were inert even under extreme conditions. These last results served to eliminate any direct electronic correlations. It appears quite possible that steric effects in the more highly alkylated ferrocenes may account for their inertness.

Results from these laboratories (79) likewise support the idea that the ring-metal bond of a ferrocene system is quite labile. Treatment of the optically active ketone (V) with refluxing nitromethane and AlCl_3 brought recovery of the identical ketone



but of much lower optical purity. The most likely mechanism for this racemization involves scission of the substituted ring-metal bond, since the other possible mechanisms of racemization, which involve reversible Friedel-Crafts alkylation and acylation, are unlikely. Examples of the non-reversibility of both acyl- and alkylferrocenes under Friedel-Crafts conditions have been published (23). These results are significant in that they demonstrate exchange of a substituent containing an electron-withdrawing group. No data are available on the rate of exchange of the unsubstituted ring in ketone (V), although the trends observed in the systems previously discussed suggest that this rate of exchange should be much faster than that of the substituted ring.

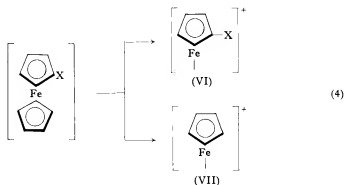
Although 1,1'-diethylferrocene has been shown not to undergo synproportionation with ruthenocene, favorable results have now been obtained with RuCl_3 (18). Ruthenocene and 1,1'-diethylruthenocene were isolated from the reaction of ferrocene and 1,1'-diethylferrocene, respectively, upon

heating with RuCl_3 for 1–2 days at 250 °C. This provided the first example of a ligand-exchange reaction to a different metal.

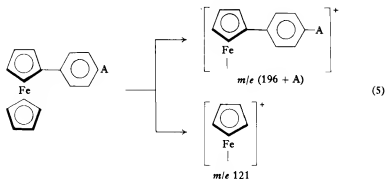
From the studies cited, no quantitative conclusions can be reached concerning the effect of substituents on the strength of the ring–metal bonds in substituted ferrocenes. However, if it is assumed that the ease of ligand exchange reflects the relative strength of the ring–metal bonds, then, qualitatively, electron-donating groups appear to weaken the bond whereas electron-withdrawing groups serve to strengthen the ring–metal bond.

B. Mass Spectroscopy

The mass spectra of many substituted ferrocenes have been published and various pathways have been postulated to account for the fragments observed (10, 14). The mass spectrum of ferrocene itself exhibits a high abundance for the m/e 121 peak which has been attributed to the fragment $[\text{C}_5\text{H}_5\text{Fe}]^+$ presumed to arise from cleavage of the ring–metal bond. Substituted ferrocenes then offer two possible fragmentation paths involving cleavage of the ring–metal bond [Eq. (4)]. The relative intensities of each fragment observed should reflect the strength of the individual



ring–metal bonds. Thus a ferrocene with a group which strengthens the substituted ring–iron bond should exhibit a greater abundance for fragment (VI) than for fragment (VII) in its mass spectrum. The converse would, of course, be true for those ferrocenes containing bond-weakening substituents. For example, mass spectral analysis of several monosubstituted ferrocenes containing a para-substituted phenyl group [Eq. (5); Table IX]



indicated the presence of such a substituent effect within this particular system (67). Phenylferrocene itself exhibited a larger abundance of the m/e

TABLE IX

RATIO OF SUBSTITUTED RING-IRON CLEAVAGE TO UNSUBSTITUTED RING-IRON CLEAVAGE FOR PARA-SUBSTITUTED PHENYLFERROCENE^a

Substituent A	$\frac{\% m/e (196 + A)}{\% m/e (121)}$
NH ₂	0.45
H	0.63
C ₆ H ₅	0.19
NO ₂	0.0

^a Rinehart (67).

121 fragment than of the $m/e (196 + A)$ fragment. Thus the phenyl group must weaken the substituted ring-iron bond. If the withdrawing strength of the phenyl ring was increased by placing another phenyl or nitro group in the para position, the relative amount of substituted ring-iron bond cleavage increased. However, the *p*-aminophenyl group also exhibited a $(196 + A)/121$ ratio less than that observed for the unsubstituted phenyl group itself. Possibly the inductive electron-withdrawing effect of the amino group is dominating in this particular case, although it is more likely that some secondary fragmentation processes are taking place which serve to diminish the $(196 + A)$ fragment.

Preliminary data are also available on mass spectral correlations of several mono- and 1,1'-disubstituted ferrocenes where no phenyl group intervened between the substituent and the ferrocene ring. Results of this study are tabulated in Table X. The weakening effect of the acetyl and acid groups on the substituted ring-iron bond is clearly demonstrated in the compounds

TABLE X
RATIO OF $[C_5H_4XFe]$ PEAKS IN THE MASS SPECTRA
OF MONOSUBSTITUTED AND 1,1'-DISUBSTITUTED FERROCENES^a

Compound	Fragment A $m/e [C_5H_4XFe]^+$	Fragment B $m/e [C_5H_4XFe]^+$	Experimental ratio of A/B
$\frac{\text{---COCH}_3}{\text{Fe}}$	163 (X = COCH ₃)	121 (X = H)	0.29
$\frac{\text{---NHCOCH}_3}{\text{Fe}}$	178 (X = NHCOCH ₃)	121 (X = H)	0.97
$\frac{\text{---COCH}_3}{\text{FeNHCOCH}_3}$	163 (X = COCH ₃)	178 (X = NHCOCH ₃)	0.095
$\frac{\text{---CO}_2\text{H}}{\text{FeCH}_3}$	165 (X = CO ₂ H)	137 (X = CH ₃)	0.15

^a Rinehart (67).

containing these groups (Table X). Interestingly, the acetylated amino-ferrocene exhibits hardly any preferential cleavage of either of its ring-iron bonds.

The data from these mass spectral studies suggest that electron-withdrawing groups weaken the substituted ring-iron bond. The data for electron-donating groups are more equivocal, although there is some ground for suggesting that such groups strengthen the substituted ring-iron bond (the ratio of the two cleavage products for the 1-acetyl-1'-acetylaminoferrrocene is less than that for acetylferrocene itself) (Table X). These conclusions are opposite to those obtained from the ligand-substitution study (Section III,A), in which electron-withdrawing groups appeared to strengthen the substituted ring-iron bond.

IV

**SUBSTITUENT EFFECTS ON THE
HETEROATOM. OXIDATION-REDUCTION POTENTIALS**

It is well known that ferrocene and related metallocene compounds undergo reversible oxidation by a variety of chemical oxidants. The particular ease with which ferrocene undergoes oxidation to its ferricinium cation allows one to determine the effect of a series of substituents on the oxidation potential of the ferrocene system. Thus a sensitive probe is available for determining the electronic effect a substituent has on the iron heteroatom and a device is made available by which one might elucidate the mechanism by which such an effect is transmitted from the substituent to the iron atom in the ferrocene system. It is unfortunate that lack of suitable derivatives has precluded similar studies in systems containing other transition metal atoms.

The most widely employed methods of following oxidation of ferrocene to the ferricinium cation involve use of potentiometric, chronopotentiometric, and polarographic techniques (35, 59, 66). However, experimental difficulties within the polarographic method limit the usefulness of this method. Consequently, potentiometric and chronopotentiometric oxidations are most usually employed in these studies (21).

The first attempt to investigate substituent effects by this oxidation technique was that of Kuwana and co-workers (38). They observed that the quarter-wave potential determined by chronopotentiometry varied considerably with the nature of the substituent. It was quite evident from their data that ferrocenes which contained electron-donating groups were more easily oxidized than ferrocene and those which contained electron-withdrawing groups were more resistant to oxidation than ferrocene itself. These results were not surprising since it was known that amino- (1) and hydroxyferrocene (5) suffered oxidation within a very short period when exposed to the atmosphere.

Several amplifications of the results of Kuwana have since been published. Free-energy relationships between $E_{1/4}$ values and various substituent constants have been employed in an attempt to characterize more quantitatively the nature of the electronic effect transferred from the substituent to the reaction site, in this case the iron atom. Such studies have brought conclusions that the primary mode of transmittance of these effects involves inductive (38) and combined inductive-resonance parameters (25, 28, 29,

43). Evaluation of these constants has been designated by the correlation coefficients. Misleading conclusions are often obtained from these coefficients. This was clearly indicated in the Hall-Russell study (28), in which the same degree of correlation (0.995) was obtained with the $E_{1/4}$ values and either σ_p or σ_m constants by using only a selected group of substituted ferrocenes in each plot. However, when these groups of ferrocenes were combined, significant differences in the overall correlation coefficient of these two Hammett constants were observed (0.920 for σ_m and 0.983 σ_p). The most comprehensive list of substituted ferrocenes examined by this technique is that of Hall and Russell (43); this is included here as Table XI.

As suggested by Kuwana (38), substituent effects in disubstituted ferrocenes may be additive. This point was demonstrated by Gubin and co-workers (62) by the comparison of the observed potentials from dichromate oxidations of a series of 1,1'-symmetrical and unsymmetrical disubstituted ferrocenes with the calculated potential value from the equation

$$E_{\text{calc}} = E_F + \Delta E_X + \Delta E_Y$$

where E_F is the potential of ferrocene alone; E_X , the potential of ferrocene with X substituent; and E_Y , the potential of ferrocene with Y substituent. The difference between the calculated and observed values was at the most 4.1%. Thus Gubin concluded that the effects in operation in these ferrocene systems were additive and that in such oxidations a substituent in the second ring exerted no influence on the magnitude of the interaction of the substituent in the first ring.

To examine the idea of a long-range transmittance of electronic effects to the iron atom, several ortho-, meta-, and para-substituted phenylferrocenes were prepared and their oxidation potentials studied potentiometrically by oxidation with dichromate (44). Little and associates concluded from the *o*-phenylferrocenes that steric effects are relatively unimportant and do not much influence the potential. Likewise, Mason and Rosenblum (47) observed good correlation between potentials for a series of *p*-phenylferrocenes and σ_p constants.

To sum up the body of evidence concerning the effect of a substituent on the iron atom in the ferrocene system, several points should be stressed. First of all, the substituents can be classified as those which cause the system to be more easily oxidized than ferrocene itself (electron-donating groups)

TABLE XI

CHRONOPOTENTIOMETRIC QUARTER-WAVE POTENTIALS FOR REVERSIBLY OXIDIZED FERROCENE DERIVATIVES IN ACETONITRILE AT 25°C, RELATIVE TO THE QUARTER-WAVE POTENTIAL FOR FERROCENE^a

Substituents	$\Delta E_{1/4}$	$\Sigma \sigma_m$	$\Sigma \sigma_p$
<i>$\Delta E_{1/4}$ (silver-silver perchlorate electrode)^b</i>			
1,1'-Di(ethoxycarbonylamino)	-0.139	0.204	-0.172
1,1'-Di(methoxycarbonylamino)	-0.137	0.204	-0.172
Methoxycarbonylamino	-0.070	0.102	-0.086
Acetamido	-0.068	0.102	-0.086
Methoxy	-0.058	0.115	-0.268
3-Acetyl-1,1'-dimethyl	0.148	0.238	0.162
1'-Acetyl-1-methoxycarbonylamino	0.157	0.478	0.416
1'-Acetyl-1-acetamido	0.171	0.478	0.416
2-Acetyl-1-acetamido	0.250	0.478	0.416
1,1'-Dibromo	0.317	0.782	0.464
Cyano	0.375	0.560	0.660
1'-Acetyl-1-bromo	0.406	0.767	0.734
1'-Acetyl-1-chloro	0.427	0.749	0.729
1,1'-Diacetyl	0.488	0.752	1.004
1'-Acetyl-1-cyano	0.598	0.936	1.162
<i>$\Delta E_{1/4}$ (standard calomel electrode)^c</i>			
1,1'-Diethyl	-0.115	-0.140	-0.302
1,1'-Dimethyl	-0.100	-0.138	-0.340
Ethyl	-0.061	-0.070	-0.151
Methyl	-0.060	-0.069	-0.170
Hydrogen	0.000	0.000	0.000
Trimethylsilyl	0.005	-0.040	0.070
1,1'-Di(trimethylsilyl)	0.005	-0.080	-0.010
Phenyl	0.028	0.060	-0.010
1,1'-Diphenyl	0.055	0.120	-0.020
Iodo	0.042	0.352	0.180
1'-Ethyl-1-carboxy	0.182	0.300	0.300
Carboxy	0.240	0.370	0.450
Carbethoxy	0.241	0.370	0.450
Benzoyl	0.260	0.343	0.429
Acetyl	0.255	0.376	0.502
1,1'-Dicarboxy	0.453	0.740	0.900
1'-Acetyl-1-carboxy	0.466	0.750	0.950

^a Little *et al.* (43).

^b $E_{1/4}$ for ferrocene was determined to be 0.063 V.

^c The $\Delta E_{1/4}$ data cited are taken directly from the appropriate tables in reference (44). In some instances, these data are averages of values reported in references (38) and (29), as well as in reference (44).

and those which increase the stability of the ferrocene system towards oxidation (electron-withdrawing groups). Secondly, the effects are transmitted to the iron atom in a manner similar (from a resultant point of view) to that by which electronic effects are transmitted in para-substituted benzoic acids. Lastly, the effects are additive and for the most part act independently of one another.

V

INTERANNULAR ELECTRONIC EFFECTS

For metallocenes it seems apparent that any perturbing electronic effect transmitted from one ring to the other ring would contribute significantly to the overall electron distribution within the molecule. In order to obtain a better understanding of bonding in metallocenes, many authors have tried to devise systems which would allow an estimate to be made of the transmittance of any effect through the metal atom to the other ring. Three main approaches have been applied to such estimations:

- (1) Relative site reactivities of the various ring positions towards electrophilic attack
- (2) Spectroscopic studies.
- (3) Dissociation constants of heteroannular disubstituted ferrocenes.

These studies have all reached the same conclusion, namely, that a small but significant electronic effect can be transmitted from one ring to the other, apparently through the metal atom.

A. *Relative Site Reactivities*

It is well known that electron-donating groups attached to benzene greatly enhance the ring's reactivity towards electrophilic substitution reactions, whereas electron-attracting groups decrease such reactivity markedly. Like most aromatic systems, ferrocene undergoes electrophilic substitution reactions readily. Care must be exercised because of the ease of oxidation of ferrocene to the ferricinium cation. Thus ferrocene cannot be nitrated, chlorinated, or brominated. Acetylation under a variety of conditions (63) has been successful, however. Under intensive Friedel-Crafts conditions further acetylation of acetylferrocene took place exclusively

in the unacylated ring. This deactivating effect of the acetyl group on the substituted ferrocene ring has been fully discussed by Rosenblum and co-workers (69). They observed that ferrocene underwent acetylation 1.7×10^4 times faster than acetylferrocene. Similar results were obtained for the acylation of chloro-, bromo-, iodo-, and cyanoferrocene, where substitution occurred only under the most severe conditions and solely in the unsubstituted ring (27).

The relative site reactivities toward acetylation for the alkylferrocenes were given in Table I (Section II,A2) (34). It was observed that the alkyl group activated the substituted ring with respect to the unsubstituted ring. Reevaluation of these data, using the 3-position as reference, is shown in

TABLE XII
RELATIVE RATE OF ACETYLATION OF ALKYLFERROCENES

Substituent	1'-Position ^{a, b}
CH ₃	0.63
CH ₂ CH ₃	0.53
CH(CH ₃) ₂	0.42
C(CH ₃) ₃	0.30

^a Benkeser *et al.* (4).

^b Relative to the 3-position taken as 1.0.

Table XII (4). The reactivity at the 1'-position decreases through the series from methyl to *tert*-butyl. The 3-position to 1'-position ratio could decrease through the series in two ways, namely, the 3-position reactivity could increase or the 1'-position reactivity could decrease. In the absence of further data, no distinction can be made between these two possibilities.

B. Spectroscopy

1. NMR

Relative site reactivities predict that for monosubstituted ferrocenes containing strongly electron-withdrawing groups the unsubstituted ring should possess a greater electron density relative to the substituted ring; for electron-donating groups the opposite would be true, namely, the

electron density in the substituted ring should be greater than that in the unsubstituted ring. Unfortunately, clear-cut electrophilic substitution data are not available to support this latter contention. Results of spectroscopic examinations, on the other hand, appear to support these correlations. For example, if one assumes that the extent of shielding in the PMR spectra of ring protons in aromatic molecules is a valid estimate of the electron density at that position, then acyl-type ferrocenes would be thought to exhibit their greatest electron density in the unsubstituted ring. Recently Gubin and co-workers (16) have shown that the chemical shift of the various protons in the PMR spectra of a series of monosubstituted ferrocenes was highly dependent upon the nature of the substituent (see Table II; Section II,B,1). A plot of the shielding values (with respect to ferrocene) of the unsubstituted ring of nine monosubstituted ferrocenes versus Taft's inductive substituent constant showed very good correlation, with a correlation factor of 0.978. From this the authors concluded that such effects are transmitted from the substituent through the substituted ring and the metal atom to the unsubstituted ring primarily by an inductive mechanism and that any transmittance by a resonance contribution remains essentially constant. However, significant deviation from this line was observed for the shielding values of chloro- and iodoferrocene. This may be due to a field effect or a contact interaction with the respective halogen.

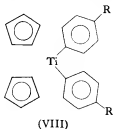
Work by Nesmeyanov and co-workers (17) also supported the idea of inductive transmittance of such effects by showing that a large number of heteroannularly disubstituted ferrocenes display PMR spectra which apparently obey an additivity rule. These authors compared the observed and calculated chemical shift values for a series of symmetrical and unsymmetrical 1,1'-disubstituted ferrocenes for which the calculated value was obtained by adding the shielding value (versus ferrocene) of the unsubstituted ring of a monosubstituted ferrocene to the average chemical shift of the 2,5- and 3,4-position protons. This new value gave fairly good correlation with the average ring proton chemical shift for the corresponding 1,1'-compound if no direct interaction between the substituents was observed.

Butter and Beachell (11) utilized a somewhat different method of estimating the electron density apportioned to the unsubstituted ring. A plot of shielding values of eight monosubstituted ferrocenes vs. Hammett's σ constants was obtained for both the substituted and unsubstituted ring protons. From the slopes of these plots the authors obtained ρ values of

0.90 and 0.20 for the substituted and unsubstituted ring protons, respectively. The ratio of these two values in percentage terms was 22%, which was taken as an estimate of the transmission of the effect through the ferrocene nucleus. In a similar manner a series of para-substituted arylferrocenes yielded a transmission value of 14%. Thus, it was concluded that the effect falls off somewhat with an increase in distance between the substituent and the site of measurement.

It has also been observed that the regression lines for 1'- and 2-substituted methylferrocenes, obtained from the plot of the chemical shift values of the $-\text{CH}_3$ protons vs. σ_p constants, have different slopes (70). This change was attributed to the difference in the transmissibility of the electronic effect through the ferrocene nucleus. The ratio of the slopes (in percentage terms) gave a value of 28%, which agreed reasonably well with the value obtained by Butter and Beachell (22%) (11).

The PMR spectra of certain related titanocene derivatives have been similarly studied and analyzed for transmission effects. For the para-substituted diaryltitanocenes (VIII), 21% of the effect from the substituent was estimated to be transmitted through the metal atom to the cyclopentadienyl ring (3, 11). It is interesting that this value is higher than that obtained for the arylferrocenes (14%). This is not, however, unexpected since the aryl group of titanocene is directly bonded to the metal.



2. Infrared

Infrared studies have shown dependence of the carbonyl absorption value of a series of heteroannularly substituted ferrocene carboxylic acids and their methyl ethers on changes in the substituent in the other ring. Nesmeyanov and co-workers (31) have detected a shift to lower frequencies of $\nu_{\text{C=O}}$ values with increasing electron donation. For example, the carbonyl absorption was observed to be 1704 cm^{-1} for 1'-sulfurfluoroferrrocene-carboxylic acid, but when the substituent was a methyl or *tert*-butyl the

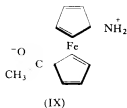
frequency was shifted to 1672 cm^{-1} . More recently, Busby (12) has offered a more quantitative description of these infrared effects. A series of eleven 1'-substituted acetylferrocenes were prepared, with the 1'-substituents ranging from very strong electron donors ($-\text{NH}_2$, $-\text{OCH}_3$) to strong electron acceptors ($-\text{COPh}$, $-\text{CN}$). The infrared spectra of these acetylferrocenes apparently experienced an electronic effect similar to that of the compounds reported by Nesmeyanov (31), that is, a shift to higher frequencies for those ferrocenes containing electron donors. Upon plotting the carbonyl absorption versus the various possible Hammett σ constants, the correlation coefficients given in Table XIII were obtained. Notice was taken that σ_m

TABLE XIII
CORRELATION OF C=O ABSORPTION AND
HAMMETT CONSTANTS OF 1'-SUBSTITUTED ACETYLFERROCENES^a

σ Constant	Correlation coefficient
σ_p	0.9806
σ^+	0.9607
σ_m	0.9121
$\left(\frac{\sigma_m + 2\sigma_p}{3}\right)$	0.9779

^a Busby (12).

evidently did not provide a good estimation of this electronic effect, whereas σ_p provided good correlation, i.e., these effects are most similar to those experienced in para-substituted benzoic acids, which are made up of both polar and resonance effects. Since σ^+ did not correlate as well as σ_p , a direct resonance interaction of the type illustrated in structure (IX) must not play



an important part in the transmission of these effects. More convincingly, Busby has demonstrated that if the direct interaction is occurring to any extent, the slope of the plot for the compounds containing electron-donating groups should be the same as that obtained from strongly electron-withdrawing groups. The following results were obtained for those plots employing σ^+ values:

Slope	Substituents
7.85	$-\text{NH}_2$, $-\text{OCH}_3$, $-\text{NHCOCH}_3$, $-\text{C}_2\text{H}_5$
15.77	$-\text{Br}$, $-\text{CO}_2\text{C}_2\text{H}_5$, $-\text{COC}_6\text{H}_5$, $-\text{COCH}_3$

Spectroscopic studies thus revealed that electronic effects are transmitted through the iron atom and are comparable to those effects experienced in para-substituted benzoic acids and that apparently no direct resonance interaction between the substituents exists. Recent ESR data have provided both positive (45) and negative (15) evidence for such a resonance interaction.

C. Dissociation Constants of Ferrocenoic Acids

Dissociation constants of heteroannularly disubstituted ferrocenoic acids have been employed as a means of measuring the effect of a substituent in one ring on the electron distribution in the other. One would expect those substituents which withdraw electron density to stabilize the anion formed on ionization, thereby increasing the acidity of the substituted ferrocenoic acid. This is indeed the result observed by Nesmeyanov and Reutov (52). Over a decade ago these authors found that 1'-acetylferrocenoic acid was 2.4 times as strong an acid as ferrocenoic acid itself, whereas the latter is 3.3 times stronger than 1'-ethylferrocenoic acid.

A more quantitative description of such effects in the 1'-substituted ferrocenoic acids was provided by Little and Eisenthal (41). Upon plotting the $\text{p}K_{\text{A}}$ of six heteroannularly disubstituted ferrocenoic acids versus Hammett's σ_{p} constant, a satisfactory straight line was observed with a slope of 0.74. From this one would expect both the resonance and inductive mechanisms to play a role in the transmission of the effect from the substituent to the acid site. Similarly, the kinetics of the reaction of several heteroannularly disubstituted ferrocenoic acids with diphenyldiazomethane led the same authors to conclude that σ_{p} seemed to give the best estimate of the effect transferred from one ring to the other (42).

In contrast to the results indicating the similarity in the electronic effects transmitted in the heteroannularly substituted ferrocenoic acids to those of *p*-substituted benzoic acids, others have shown that an equally satisfactory correlation existed between these acids and σ_p , Taft's inductive parameter. The importance of the inductive nature of these substituents is demonstrated by the acid-strengthening affect of the methoxy group in methoxyferrocenoic acid (22). In support of this contention that an inductive effect predominates, free-energy relationships of the solvolysis of several heteroannularly disubstituted methylferrocenylcarbonyl acetates were found to be best correlated with $[(\sigma_m + 2\sigma_p)^3]$ which suggested that σ_p overestimated such resonance effects (26).

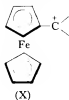
In view of the studies presented above, it becomes quite apparent that substituent effects are transmitted through the iron atom to the other ring in the ferrocene system and they appear to be electronic in nature. This effect is apparently transmitted by both a resonance and an inductive mechanism. Consensus on quantitative estimates of the extent of each effect is still lacking, however.

VI

THE ELECTRONIC INFLUENCE OF FERROCENYL AND RELATED GROUPS AS SUBSTITUENTS

In the previous sections the various influences of substituents on metallocenes and related molecules have been examined. To complete a study of the electronic nature of these molecules, it remains that their behavior as substituents themselves be discussed.

The very strong electron-donating power of the ferrocene nucleus is clearly demonstrated in the extraordinary stability of the α -ferrocenyl carbonium ion (X). Questions have been raised concerning the mode of stabilization of such ions, i.e., (1) whether the π -orbitals of the ring overlap the empty *p*-orbital (resonance), (2) whether the *d*-orbitals on iron participate or overlap the empty *p* orbital, and (3) whether there is ring movement.



These ions have received considerable attention and have been extensively reviewed (13). The chemistry of such ions is thus outside the scope of this review; additional information may be found in the latest papers of Nugent and Richards (58). However, the more quantitative aspects of the electron donor properties of the ferrocenyl and related groups, such as those provided by determination of their Hammett σ -constants, are most appropriate for inclusion here.

Relatively few quantitative estimations of the electron donor properties of the ferrocene nucleus have appeared in the literature. A paper by Little, Berry, and Kannan (40) reported measurements of the basicities of ferrocenylazobenzenes, a study which was complicated by protonation of the ferrocenyl group. Arnett and Bushick (2) provide some semiquantitative estimates of σ and σ^+ for metallocenyl nuclei. More recently, a most informative study by Nesmeyanov and co-workers (51, 61) on the electroic nature of the ferrocenyl group has provided Hammett σ values for the ferrocenyl group derived from the dissociation constants of *p*-, *m*-, and *o*-ferrocenylbenzoic acids, ferrocenecarboxylic acid, and *p*-ferrocenylphenol and from the basicity constants of *p*-, *m*-, and *o*-ferrocenylanilines and ferrocenylamine. By use of the K_A and K_B data, free-energy relationships were obtained for the ferrocenyl groups and from these the various σ -values for the ferrocenyl group were calculated (Table XIV). Similar studies of the ruthenocenyl (24) and the benzenechromium tricarbonyl (6, 7, 23) substituents have recently been published.

Both the σ_m and σ_i values in Table XIV demonstrate that the ferrocenyl group is among the strongest inductive electron donors known. In contrast to this the ruthenocenyl σ_i substituent constant reveals that this group is inductively slightly electron-withdrawing. The strong inductive donor properties of the ferrocenyl group are rendered apparent by comparison of its σ_m value (Table XIV) to that of a methyl group ($\sigma_m = -0.07$). The general polar influence of the ferrocenyl group is likewise shown to be that of an electron donor, with its σ_p value, although reaction-dependent in some cases, being comparable to that of a methyl group ($\sigma_p = -0.17$).

Relatively extensive studies have been performed on the solvolysis of several arenechromium tricarbonyl tosylates (6, 7). Comparison of the solvolysis data of the complexed and noncomplexed optically active *threo*- and *erythro*-3-phenyl-2-butyl tosylates led the authors to conclude that complexation of these tosylates inhibited phenyl and hydrogen migration, prevented racemization in the *threo* case, and reduced direct displacement

by the solvent. No extraordinary rate acceleration during solvolysis was noted. Thus, the α -carbonium ion in these complexes exhibited quite different behavior from that of the corresponding α -carbonium ion in the ferrocene examples.

Other studies of considerable interest have been performed on such systems (33, 57). Pettit *et al.* (30) had first suggested that the chromium tricarbonyl-complexed benzyl cation was extraordinarily stable. Trahanovsky and Wells (80) have quantitatively estimated the difference of pK_R^+ for

TABLE XIV
 σ VALUES OF METALLOCENYL AND RELATED GROUPS

Group	σ_p	σ_m	σ_t	σ^*	σ_p^+
$C_5H_5FeC_5H_4-$	-0.18 ^a	0.15 ^a	-0.05 ^b	-0.33 ^b	-0.55 ^b
	-0.10 ^b	—	-0.08 ^c	—	-0.68 ^b
	-0.05 ^c	—	-0.12 ^c	—	-0.65 ^e
	-0.03 ^c	0.00 ^e	—	—	—
$C_5H_5RuC_5H_4-$	-0.05 ^b	—	+0.04 ^b	+0.26 ^b	-0.44 ^b
	—	—	—	—	-0.69 ^b
$[C_5H_5FeC_5H_4-]^*$	+0.29 ^f	+0.29 ^f	+0.30 ^b	+1.85 ^b	—
$(CO)_3CrC_6H_5-$	+0.18 ^d	—	+0.31 ^d	+1.96 ^d	-0.15 ^d
	+0.23 ^d	—	+0.21 ^e	—	—

^a Nesmeyanov *et al.* (51).

^b Gubin and Lubovich (24).

^c Perevalova *et al.* (61).

^d Gubin and Khandkarova (23).

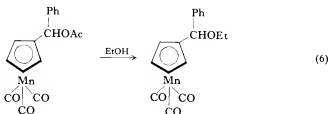
^e Khandkarova *et al.* (32).

^f Little *et al.* (40).

the complexed and free benzyl cation and have found that the chromium tricarbonyl-complexed benzyl cation is greater than 5.5 pK units more stable than the uncomplexed benzyl cation. On the other hand, estimation of the thermodynamic stabilities of some α -substituted α -hydroxybenzyl cations complexed with the chromium tricarbonyl group revealed the variability of the stabilizing effect of this group; some of the ions examined were found to be less stable than their uncomplexed counterparts (81).

A third system, the cymantrenylmethyl carbonium ion, has been briefly examined (46). It appears to possess some carbonium ion-stabilizing ability

in that α -acetoxybenzylcymantrene could be transformed in 55% yield into the corresponding ether by 3-day reflux in ethanol.



The ferrocene analog had previously been reported to require only 3 hours. Interestingly, benzhydriyl acetate after 3 days gave no other product under the same conditions.

From Table XIV it can be seen that the electronic natures of the various cyclopentadienyl complexes examined here are not uniform, i.e., ferrocene is a strong electron donor, and ruthenocene and cymantrene are only moderately so, while the benzenechromium tricarbonyl system can apparently exhibit both donor and acceptor properties. There is no reason to think that the interaction of a metallocenyl group with a reaction site would be the same as that of benzenechromium tricarbonyl group. It is interesting that a substituted benzene system, when complexed by a chromium tricarbonyl moiety, does not behave in a manner similar to the uncomplexed system. Gubin has recently studied several cases where there were no striking differences in the behaviors of complexed and uncomplexed benzene systems (21). However, in several instances there were inconsistencies. Unfortunately, no data are available on substituted cyclopentadienide ion systems so that a comparison of the electrical properties of the complexed and uncomplexed ligand might be made. Thus, assessment of electronic effects in metallocene systems should be made on an individual basis and analogies between systems should be made only after the most careful scrutiny.

VII CONCLUSION

Most of the data concerning ferrocene electronic effects correlate rather well. Ferrocene emerges as a system which homoannularly allows electron withdrawal to take place principally from the 2-position and secondarily

from the 3-position. For electron-donating substituents, the principal donation is to the 3-position. However, some exceptions to this last statement are known from relative site reactivity data. Electron density is also donated to or withdrawn from the ring-metal bond by a substituent. For electron-donating substituents the bond strength is evidently increased, while the converse is true for electron-withdrawing substituents. This does not correlate with the results from ligand exchange, but we feel the ionic nature of this process brings factors into play that cannot be appropriately evaluated at present. The ligand-exchange order may represent a kinetic effect; it is possible that a kinetic effect may also explain some of the discrepancies in the relative site reactivity data. Electronic effects in ferrocene are also possible over greater distances. A direct interaction between the substituent and the iron atom is well documented. Lastly, electron density changes are manifested to a slight extent in the unsubstituted ring of substituted ferrocenes.

Electronic effects in related organometallic π -complexes emerge less clearly. Those complexes of titanium, iron, cobalt, manganese, and chromium which have been studied do exhibit certain electronic effects, although no such complex has been defined nearly as well as ferrocene itself. In several instances, close correlation between these systems and the ferrocene system seems to exist. However, as pointed out earlier, analogous assignments between various π -complexed metal systems cannot be made with certainty. Our present state of knowledge in this area does not eliminate the possibility that complexation by the different metal atoms might influence the electronic properties of a particular ligand in subtle, but different ways.

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Nitrogen Groups in Metal Carbonyl and Related Complexes

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I. Introduction	115
II. Organonitrogen Derivatives	117
A. Amino Derivatives	117
B. Ureylene Derivatives	121
C. Carbamoyl Derivatives	122
D. Diazo Derivatives	125
E. Azido and Nitrene Derivatives	129
F. Azo Derivatives	131
G. π -Bonded Heterocyclic Derivatives	138
H. Nitrile Complexes	141
I. Dialkylcyanamide Derivatives	151
J. Nitroso and Nitroxide Derivatives	153
K. Schiff Base Derivatives	154
L. Phosphorimide Derivatives	164
M. Aminocarbene and Related Derivatives	165
N. Aminoborylene Derivatives	167
III. Derivatives of Inorganic Nitrogen Groups	168
A. Cyano Derivatives	168
B. Cyanogen Derivatives	173
C. Cyanato Derivatives	173
D. Fulminato Derivatives	176
E. Thiocyanato Derivatives	177
F. Selenocyanato Derivatives	180
G. Nitrate Complexes	182
H. Nitro and Nitrito Derivatives	183
I. Azido Derivatives	184
References	186

I

INTRODUCTION

The course of the reactions of metal carbonyls with nitrogen bases leading either to disproportionation or to carbonyl substitution has been recognized since the very early work on metal carbonyls (337)¹. Since that

¹ See the article by W. Hieber in Volume 8.

time many new types of carbonyl derivatives have been treated with neutral nitrogen bases and consequently an immense number of such derivatives is now known. Stabilization of the metal-carbonyl bonds through increased $d\pi-\pi^*$ bonding, and the pattern, stereochemistry, and mechanism of the substitution process have been extensively studied and reviewed (2, 114). Current interest is more concerned with the versatility of the bonding of nitrogen groups, particularly when nitrogen is part of a π -system, or the nitrogen donor is a captured reactive intermediate. Although unsaturated organonitrogen molecules do not undergo hydroformylation, metal carbonyls do catalyze cyclization and/or carbonylation processes. An excellent review has been given by Rosenthal and Wender (412), and although this subject will not be treated in the present review, many complexes discussed will be relevant, and possibly are intermediates in the reactions. Reviews have also appeared on molecular nitrogen complexes (15, 87, 125, 363), nitrosyls (129, 238, 286), Lewis base derivatives (21, 337, 347), tetracyanoethylene complexes (29, 408), tricyanomethyl derivatives (29), isocyanides (335), dithiolates and related complexes (154, 345), and hydrazine complexes (88). These classes of complexes have been omitted in general from this review.

Natural division into two sections occurs, namely, (1) organonitrogen derivatives, and (2) derivatives of inorganic nitrogen groups. Most groups discussed form metal-nitrogen bonds in at least one type of bonding mode, but the bonding of the other groups to the metal is influenced to such a large extent by the nitrogen atom(s) that they have also been included.

The bonding and properties of the groups are so diverse that preliminary discussions of general properties, synthetic routes, bonding, spectroscopic features, mechanisms of reaction, and stereochemistry are not appropriate, and the reviewer has preferred to include the relevant data in the various sections. Detailed reviews concerned specifically with these aspects and with the main principles and features of metal carbonyl complexes in general are numerous, and occasional references to nitrogen derivatives can be found in them (1, 2, 21, 43, 117, 146). Emphasis here is placed on the coordinated nitrogen groups.

List of Abbreviations

Ph	C ₆ H ₅	bipy	2,2'-Bipyridyl
Me	CH ₃	<i>o</i> -phen	1,10-Phenanthroline

Et	CH ₃ CH ₂	diphos	Bis(diphenylphosphino)-ethane
Ar	Arene	en	Ethylenediamine
γ -pic	γ -Picoline	<i>p</i> -fan	<i>p</i> -Fluoroaniline
<i>p</i> -tol	<i>p</i> -Toluidine	pz	Pyrazolyl
azb	Azobenzene	R(pz) ₃ B ⁻	Tri(pyrazolyl)borate

Bond distances and angles recorded in diagrams are given in angstrom units and degrees, respectively.

II

ORGANONITROGEN DERIVATIVES

A. Amino Derivatives

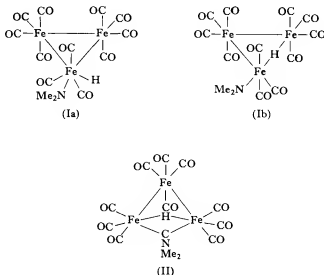
Interest in amino complexes has been stimulated by the problem of nitrogen fixation using transition metal organometallic systems and subsequent conversion to ammonia under reducing conditions (363). Both amino- and imino-bridged species are considered to be intermediates in the reaction of nitrogen with the nitrogen fixation system (π -C₅H₅)₂TiCl₂/EtMgBr (94), but attempts to simulate the process using more robust transition metal systems were not successful. Neither reactions of nitrogen with carbonyl hydrides, nor reactions of hydrogen with carbonyl nitrogen complexes have been achieved (363).

1. Complexes Containing Terminal Amino Groups

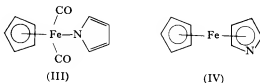
Carbonyl complexes with terminal amino groups are well established but not numerous because of the tendency of nitrogen to use its lone-pair electrons to bond to a second metal atom.

Hydrazine provides both coordinated nitrogen and amino groups in reactions with phosphine-substituted rhenium complexes. *cis*-[Re(CO)₄LBr] and *trans*-[Re(CO)₃L₂Br] (L = Me₃PPh) gave [Re(CO)₃L(N₂)(NH₂)] and [Re(CO)₂L₂(N₂)(NH₂)], respectively, but no reaction could be achieved with the *cis*-disubstituted halide complex even under drastic conditions (352). Treatment of [Fe₃(CO)₁₂] at 80°C with benzoyl chloride in dimethylformamide solution, followed by acid hydrolysis of the product, yielded a derivative originally formulated as [HFe₃(CO)₁₁NMe₂] and assigned structures (1a) or (1b) on the basis of IR and ¹H NMR studies (410). A later

Mössbauer and mass spectroscopic study resulted in its reformulation as $[\text{HFe}_3(\text{CO})_{10}\text{CNMe}_2]$, and assignment of structure (II), formally based on that of $[\text{Fe}_3(\text{CO})_{12}]$ with replacement of bridging carbonyl groups by hydrogen and $>\text{CNMe}_2$ groups (229).

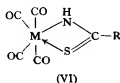
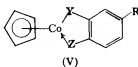


Potassium salts of pyrrole, 2-acetylpyrrole, 1,2,3,4-tetrahydrocarbazole, 9-carbazole, indole, imidazole, and 1,2,4-triazole react with $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}]$ to form $\sigma\text{-N}$ derivatives, e.g., $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\sigma\text{-N-pyrrolyl})]$ (III) (400, 421), shown to be intermediates in the formation of the π -complexes e.g., (IV) (400). Anions $[\text{M}(\text{CO})_5\text{L}]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) were similarly prepared from the hexacarbonyls and alkali metal derivatives of succinimide, phthalimidine, and saccharin (49).

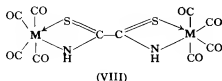
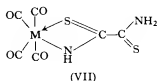


Chelate amino complexes (V; $\text{Y} = \text{NH}$, $\text{Z} = \text{O}, \text{S}$) were obtained from $[\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})\text{I}_2]$ with *o*-aminophenols and *o*-aminobenzenethiols (255). Related complexes are obtained from $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with the latter ligands

(139a), and from $[M(CO)_5X]$ ($M = Mn, Re$; $X = Cl, Br$) with *o*-aminothiophenol and 1-aminoethane-2-thiol (266, 269). Hieber *et al.* also found the latter carbonyl halides to react with the thioamines $[RC(S)NH_2]$ ($R = NH_2$,



Me, Ph) to form chelate complexes (VI; $M = Mn, R = Ph$; $M = Re, R = NH_2, CH_3, Ph$) but with dithiooxamide $[H_2NCSCSNH_2]$ both mononuclear (VII) and dinuclear (VIII; $M = Mn, Re$) complexes were isolated (266, 269).



2. Complexes Containing Bridging Amino Groups

Treatment of $[Fe(CO)_4]^{2-}$ with $NaNO_2$ or hydroxylamine under mild conditions produced a small yield of the first amino derivative $[Fe(CO)_3NH_2]_2$ (262–265), originally formulated incorrectly as the imino-bridged species (262), but later shown by mass spectrometry (221), and the X-ray crystal structure (158) to have an amino bridged structure (IX). The structure is characterized by a short metal–metal bond and small $FeNFe$ and $NFeN$ angles (Table I). Triphenylphosphine displaced one or two carbonyl groups to form the complexes $[Fe_2(CO)_5(PPh_3)(NH_2)_2]$ and $[Fe_2(CO)_4(PPh_3)_2(NH_2)_2]$, the latter undergoing oxidation with iodine to afford

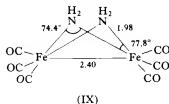


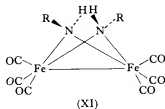
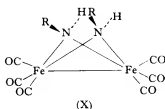
TABLE I
STRUCTURAL DATA ON NITROGEN-BRIDGED COMPLEXES

Complex	M—M (Å)	M—N (Å)	N—N (Å)	MNM°	NMN°	Dihedral ^a	References
[Fe(CO) ₃ NH ₂] ₂	2.40	1.98	2.50	74.4	77.8	104.0, 101.9 ^b	158
[π -C ₅ H ₅ Cr(NO)NMe ₂] ₂ - <i>cis</i>	2.72	2.01	—	85.0	95.1	—	112
[π -C ₅ H ₅ Cr(NO)NMe ₂] ₂ - <i>trans</i>	2.67	2.00	—	84.3	95.7	—	112
[Fe(CO) ₃ NMe] ₂	2.50	1.88	1.37	83.4	42.7	58.3, 91.1 ^b	178
[Fe ₂ (CO) ₆ (C ₁₂ H ₈ N ₂)]	2.51	1.91	1.40	81.9	42.9	89.5 ^b	177
[Fe ₃ (CO) ₉ (NMe) ₂]	2.44	1.93	—	79.2 av	71.3	96.9	176
	2.49	—	—	104.7 av	—	98.4	
	3.044	—	—	—	—	—	
[(π -C ₅ H ₅ Ni) ₃ NBu- <i>tert</i>]	2.34	1.60	—	—	—	—	390, 391
	2.37	1.73	—	—	—	—	
	2.39	1.80	—	—	—	—	
[Fe(CO) ₃] ₃ (Ph ₂ C:NN) ₂	2.46, 3.06	1.95 av	1.39	—	—	—	40
	2.43	—	—	—	—	—	
[Fe ₂ (CO) ₆ [(CH ₃ C ₆ H ₄) ₂ C:NNH] ₂]	2.40	2.00	1.40	—	—	—	33
[Fe ₂ (CO) ₆ (MeN) ₂ CO]	2.39	1.97	2.10	75.0	64.8	84.8	175, 178
	—	—	—	—	—	92.2 ^b	
[Fe ₂ (CO) ₆ (PhN) ₂ CO]	2.42	2.00	2.15	74.5	65.0	92.4 ^b	278, 404
[(π -C ₅ H ₅ Co) ₂ (<i>tert</i> -BuN) ₂ CO]	2.37	1.95	—	75.1	66.8	—	342, 343, 390, 391
[Fe ₂ (CO) ₆ (PhNC ₆ H ₄ NH)]	2.37	2.00	2.38	72.5 av	72.9	95.4 ^b	38, 39
[Fe ₂ (CO) ₆ (MeC ₆ H ₃ CH ₂ NC ₆ H ₄ Me)]	2.43	1.95	—	—	—	—	38
[Fe(CO) ₃ (MeN ₄ Me)]	—	1.83	1.32	—	—	—	174
{Fe ₂ (CO) ₆ [N ₂ C ₃ (Ph) ₃ C ₃ H ₃]}	2.39	1.92, 1.96	2.25	—	—	98.1 ^b	118
[Fe(CO) ₃ (3-Me-3-ClC ₆ H ₃ NO)] ₂	3.13	2.00	—	100	—	~ Planar	42

^a Angle between two MNM planes.

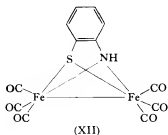
^b Angle between two MNN planes.

$[\text{Fe}(\text{CO})_2(\text{PPh}_3)(\text{NH}_2)]_2^{2+}$ (221, 272). Treatment of $[\text{Fe}(\text{CO})_3\text{NH}_2]_2$ with NO in boiling benzene results in total displacement of CO (263, 264). The related complexes $[\text{Fe}(\text{CO})_3(\text{NHR})]_2$ ($\text{R} = \text{Ph}, \text{Me}$), synthesized from $\text{Fe}_2(\text{CO})_9$ and the corresponding azides or nitromethane, were obtained in two stereoisomeric forms (X and XI; $\text{R} = \text{Me}$) arising from the arrangement of amino substituents (164). Isomerism not arising from the μ -amino



group, but from the arrangement of other groups in the complex has been reported for $[\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})\text{NMe}_2]_2$, for which the trans isomer is favored in the temperature range $25^\circ\text{--}80^\circ\text{C}$ (13). The crystal structure of both isomers indicated planar Cr_2N_2 rings (111, 112), unlike the $\text{Fe}_2\text{N}_2\text{H}_4$ system (IX) where a dihedral angle of 104° was found (158).

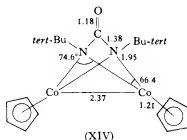
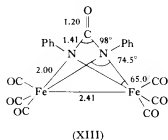
$\text{Fe}_3(\text{CO})_{12}$ reacts with *o*-aminobenzenethiol in boiling cyclohexane to form the nitrogen- and sulfur-bridged complex (XII), through loss of hydrogen from both the sulfur and nitrogen atoms (338).



B. Ureylene Derivatives

In 1964 Manuel reported that the reaction between $\text{Fe}_3(\text{CO})_{12}$ and organic azides (RN_3 ; $\text{R} = \text{Ph}, n\text{-Bu}, \text{Me}$) or isocyanates (RNCO ; $\text{R} = \text{Ph}, n\text{-Bu}, \text{Me}$) yielded $[\text{Fe}(\text{CO})_3(\text{RNCO})]_2$ (336), but later workers reformulated the complexes as $[\text{Fe}_2(\text{CO})_7(\text{RN})_2]$, and showed the presence of the ureylene group (164, 214, 278). Formation of the latter requires decarbonylation of

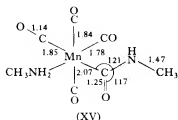
isocyanate molecules and the generation of nitrene intermediates (214). Interestingly, the phenyl compound is produced in the spontaneous decomposition of $[\text{Fe}(\text{CO})_3\text{NPh}]_2$, and the methyl compound in the reaction of $\text{Fe}_2(\text{CO})_9$ with nitromethane (164). Related intermediates were considered to be involved in the reaction of ruthenium carbonyls and PhNO_2 in the presence of H_2/CO mixtures (185). The X-ray crystal structure of $[(\text{PhNCONPh})\text{Fe}_2(\text{CO})_6]$ (XIII) indicated a normal Fe—Fe bond length for a nitrogen-bridged structure (Table I), and a small dihedral angle (94.2°) (278, 404). Other features of interest are the NCN angle (98°), which is much less than expected for sp^2 -hybridized carbon, and the long Fe—C bond (1.79 \AA) in a trans position to the metal-metal bond (others are 1.76 \AA). The X-ray crystal structure of the corresponding μ -dimethylureylene complex has also been determined (Table I). Replacement of phenyl by methyl groups produced a shortening of the Fe—N distances by $\sim 0.03 \text{ \AA}$ and again, associated with the nitrogen bridges, is a short Fe—Fe bond distance (2.42 \AA) (175). Indeed the Fe—Fe bond distances for nitrogen-bridged complexes are among the shortest known. A cobalt-ureylene complex $[(\pi\text{-C}_5\text{H}_5\text{Co})_2(\text{tert-BuNCONBu-tert})]$ (XIV) was isolated from the reaction of *N-tert*-butylsulfurimide, $(\text{tert-BuN})_2\text{S}$, with $[\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2]$, which was thought to proceed via an intermediate nitrene complex $(\pi\text{-C}_5\text{H}_5)\text{Co}(\text{CO})\text{NBu-tert}$ (342, 391). The X-ray crystal structural determination indicated a short cobalt-cobalt distance (2.37 \AA), which is 0.1 \AA smaller than that in the related acetylene complex $\text{Co}_2(\text{CO})_6(\text{C}_2\text{Ph}_2)$ (342, 343, 390, 391).



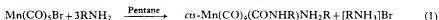
C. Carbamoyl Derivatives

Metal carbonyls, particularly cobalt carbonyl, catalyze the carbonylation of primary amines to formamides and ureas (113, 412), and for many years it was thought that the mechanism involved intermediate carbamoyl

derivatives. Angelici demonstrated that complexes of this type could be isolated from the reactions of primary aliphatic amines with $\text{Mn}(\text{CO})_5\text{Br}$. Elimination of a hydrogen atom according to Eq. (1) gave *cis*- $[\text{Mn}(\text{CO})_4(\text{NH}_2\text{R})(\text{CONHR})]$ ($\text{R} = \text{Me, Bu, iso-Pr, C}_6\text{H}_{11}$), (20, 23) shown to have structure (XV) (126). $[\text{Re}(\text{CO})_4(\text{NHR}'')(\text{CONRR}')] and $[\text{Re}(\text{CO})_4(\text{NH}_2)(\text{CONH}_2)]$ were prepared similarly (24, 61). Nucleophilic attack at a carbon atom by the amine (RNH_2 , $\text{R} = \text{H, Me}$) was thought to be the initial stage$



of the reaction. Treatment with HCl gave $[\text{M}(\text{CO})_5\text{NH}_2\text{R}]\text{Cl}$ ($\text{M} = \text{Mn, R} = \text{Me, Et; M} = \text{Re, R} = \text{H, Me}$), but regeneration of the carbamoyl complex was achieved by addition of the amine (23, 61).



The occurrence of *N*-alkylcarbamoyl complexes in the reaction of amines with $\text{Co}_2(\text{CO})_8$ was demonstrated by isolation of $[\text{R}_2\text{NCOCOC}(\text{CO})_3(\text{PPh}_3)]$ ($\text{R}_2\text{N} = \text{PrNH, } n\text{-BuNH, MeNPh, Ph}_2\text{N}$) on addition of the neutral ligand. With piperidine two complexes were identified in solution by IR spectroscopy as $[\text{C}_5\text{H}_{10}\text{NCOCOC}(\text{CO})_4]$ and $\text{C}_5\text{H}_{10}\text{NCOCOC}(\text{CO})_3(\text{C}_5\text{H}_{10}\text{NH})$ (395).

King reported the first carbamoyl derivative $[\text{R}_2\text{NCOFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{Me, Et}$), obtained as an unstable, orange, volatile, solid from the reaction of R_2NCOCl ($\text{R} = \text{Me, Et}$) with $[\text{Fe}(\text{CO})_2\pi\text{-C}_5\text{H}_5]^-$ (303). He observed the carbamoyl carbonyl stretching frequency at lower energy than for corresponding acyl groups, and suggested that the bond order is reduced by the resonance structures (XVI and (XVII), with partial



(XVI)

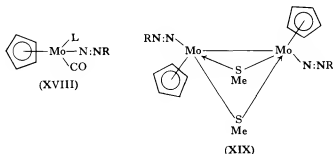


(XVII)

solid the proton may bridge the two nitrogens (180). No carbamoyl complexes were detected in the reactions of pyrrolidine with (olefin) $\text{Fe}(\text{CO})_4$ complexes or with $\text{Fe}_2(\text{CO})_9$, the simple substitution product $[\text{Fe}(\text{CO})_4(\text{C}_4\text{H}_9\text{N})]$ being formed (102).

D. Diazo Derivatives

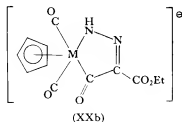
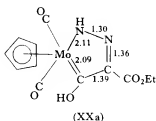
The ability of the $\text{RN}:\text{N}$ group to act as a three-electron donor to one metal atom was demonstrated initially by King, who synthesized $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2\text{N}:\text{NR}]$ (XVIII; $\text{M} = \text{Mo}, \text{W}$; $\text{R} = p\text{-R}'\text{C}_6\text{H}_4$; $\text{R}' = \text{H}, \text{Me}, \text{MeO}, \text{NO}_2$; $\text{L} = \text{CO}$) from the diazonium tetrafluoroborates and $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3]^-$. The position of ν_{CO} in the IR spectrum and the diamagnetism of the complexes were consistent with $\text{RN}=\text{N}$ groups donating three electrons, similar to the isoelectronic NO group (307, 308, 373).



Complexes (XVIII; $\text{M} = \text{Mo}, \text{W}$; $\text{R} = \text{Ph}$; $\text{L} = \text{CO}$) were synthesized also from the carbonyl hydrides $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{H}]$ and PhNHNH_2 , or $[\text{PhN}_2]\text{Cl}$ in THF at -40°C (237, 373), and shown to react with $\text{P}(\text{OPh})_3$ to form $[\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})(\text{N}:\text{NPh})\text{P}(\text{OPh})_3]$ (373). King extended the series of aryldiazo derivatives of molybdenum, noting that $\nu_{\text{NN}}(\text{max})$ usually occurred in the $1545\text{--}1530\text{ cm}^{-1}$ region, but was unable to prepare derivatives of $[\text{Mn}(\text{CO})_5]^-$, $[\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]^-$, $[\text{Co}(\text{CO})_4]^-$, $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$, and $[\text{V}(\text{CO})_6]^-$ (308). However, since certain iron and tungsten derivatives are now known (119, 237, 373), a further study of these systems is required. Replacement of carbonyl groups in (XVIII; $\text{R} = p\text{-tolyl}$, $\text{L} = \text{CO}$) with PPh_3 and Me_2S_2 , which leads to the complexes (XVIII; $\text{R} = p\text{-tolyl}$, $\text{L} = \text{PPh}_3$) and (XIX), results in an apparent lowering of ν_{NN} from 1540 cm^{-1} to 1472 and 1495 cm^{-1} , respectively, although there remains

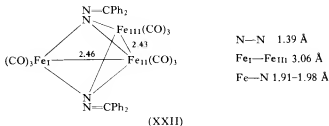
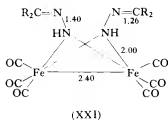
some doubt about the assignment of ν_{NN} (308). Treatment of the bis(diazo) compound, $[p\text{-C}_6\text{H}_4(\text{N}_2)_2][\text{BF}_4]_2$, with $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]^-$ gave $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{N:NPh}$ but no bridged complex, as expected. The source of the extra proton was not determined. All the carbonyl groups of (XVIII; $\text{M} = \text{Mo}$, $\text{R} = p\text{-tolyl}$) were replaced by iodine to give a complex of composition $[\pi\text{-C}_5\text{H}_5\text{MoI}_2\text{N:NR}]_n$ (308). A spectroscopic comparison of the two series of arylazo complexes $[\text{ArN:NPtCl}(\text{PEt}_3)_2]$ and $[\text{ArN:NMo}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)]$ (396) showed the latter complexes to have higher N—N bond orders (397).

Reaction of $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3]^-$ ($\text{M} = \text{Mo}$, W) with ethyl diazoacetate $[\text{HN}=\text{NCH}_2\text{COOEt}]$ gave the amphoteric complexes $\{\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2[\text{NHN:C}(\text{CO}_2\text{Et})\text{COH}]\}$ (236) shown to have the cyclic structure (XXa) in the solid state (318). The short distances within the ring indicate a degree of electron delocalization. In strong acid, the complexes protonate at the imino nitrogen, whereas with sodium hydroxide removal of the $-\text{OH}$ proton possibly occurs to form (XXb). Methylation of the cyclic anion



with MeI generates $\{\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2[\text{NMeN:C}(\text{COOEt})\text{COH}]\}$ or $\{\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2[\text{NHN:C}(\text{COOEt})\text{COMe}]\}$, which can be protonated as before at the β -nitrogen atom (236, 318).

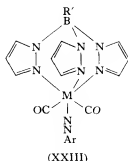
Attempts to generate diaryl carbenes using diphenyl- and di-*p*-tolyl-diazomethane in reactions with $\text{Fe}(\text{CO})_5$ or $\text{Fe}_3(\text{CO})_{12}$ gave nitrogen-containing species rather than the carbenes. Two types of compounds were isolated, the orange dinuclear complexes $[\text{R}_2\text{CHN}_2\text{Fe}(\text{CO})_3]_2$ and the black trinuclear complexes $(\text{R}_2\text{C}=\text{N}-\text{N})_2[\text{Fe}(\text{CO})_3]_3$ (33). Neither phenylbenzoyl- nor phenyldiazomethane gave stable products under similar conditions. The crystal structure of the dinuclear complex $[(\text{Ph}_2\text{CHN}_2)\text{Fe}(\text{CO})_3]_2$ (XXI) indicated a short Fe—Fe distance (2.40 Å), essentially single Fe—N bonds and sp^3 -hybridized bridging nitrogen atoms. The N—N bond distances (1.40 Å; cf. 1.12 Å in CH_2N_2) are



also consistent with single-bond formulations (33). The structure of $[\text{Fe}_3(\text{CO})_9(\text{NN}=\text{CPh}_2)_2]$ (XXII) shows the organonitrogen groups to bridge three iron atoms above and below their plane. The Fe—Fe distances indicate bonding between Fe_I — Fe_{II} and Fe_{II} — Fe_{III} , but not between Fe_I and Fe_{III} , and are thus consistent with the diamagnetism of the complex (40).

1,3-Insertion into metal-hydride bonds leads to the synthesis of the first alkylazo compounds. Treatment of $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{H}$ ($\text{M} = \text{Mo}, \text{W}$) with (trimethylsilyl)diazomethane gave red $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2\text{N}:\text{NCH}_2\text{SiMe}_3$ complexes, which for $\text{M} \equiv \text{W}$ reacts with Ph_3P in benzene (60°C) to form the monosubstitution product, $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})(\text{PPh}_3)\text{N}:\text{NCH}_2\text{SiMe}_3$. The presence of an organometallic group evidently enhances the 1,3-dipolar character of the CN_2 unit for the insertion reaction to occur, and possibly stabilizes the system through $\text{N}=\text{N}$ π -bonding to the transition metal and/or the silicon d orbitals (325). Attempted insertions of CH_2N_2 into the metal-metal bond in $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{W}-\text{SnMe}_3$, and $\text{Me}_3\text{SiCHN}_2$ into the metal-carbon bond in $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}-\text{Me}$ and into the metal-chlorine bond of *trans*-(PPh_3) $_2\text{Ir}(\text{CO})\text{Cl}$ were unsuccessful (325). Insertion of diazomethane derivatives into metal-hydrogen or metal-halide bonds was achieved for $\text{Mn}(\text{CO})_5\text{X}$ with bis(trifluoromethyl)diazomethane, the intermediate eliminating N_2 to produce $\text{Mn}(\text{CO})_5\text{C}(\text{CF}_3)_2\text{X}$ (150, 151).

The red, air-stable diazo complexes (XXIII) [$\text{M} = \text{Mo}, \text{W}$; $\text{R}' = \text{H}, \text{pz}$; $\text{Ar} = \text{C}_6\text{H}_5, p\text{-Me-}, p\text{-F-}, p\text{-NO}_2\text{C}_6\text{H}_4$] were prepared from the

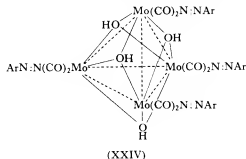


corresponding tris(1-pyrazolyl)borate anions and a diazonium salt [Eq. (2)], and shown to be much more resistant to chemical attack than the corresponding π -C₅H₅ complexes. They were unaffected by irradiation or by refluxing with MeSSMe or mineral acids. The N=N bond was not reduced



with hydrogen (Pt catalyst), nor did decarbonylation occur with PPh₃ at elevated temperatures (451, 451a). The corresponding cationic tris-(pyrazolyl)methane derivatives have also been synthesized (451a).

Treatment of Cs₄[Mo₄(CO)₁₂(OH)₄] with aryldiazonium ions in a water/ether two-phase system gave [ArN:NMo(CO)₂OH]₄ (XXIV). Although ν_{NN} occurred higher than in the corresponding π -C₅H₅ and

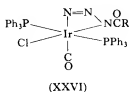
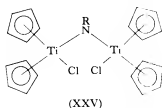


pyrazolylborate complexes, the extinction coefficient of the $\pi \rightarrow \pi^*$ transition indicated greater back-bonding to the arylazo groups in the borate complexes compared with the π -C₅H₅ analogs. It was concluded that $\nu_{\text{N:N}}$ of the arylazo ligand is not a sensitive probe for electron density on the metal. The compound [ArN₂Mo(CO)₂OH]₄ formed 1:4 adducts with

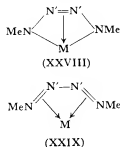
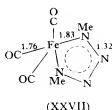
oxygen donors, the adduct site being the facial -OH groups, while *o*-phenanthroline gave $[(o\text{-phen})\text{Mo}(\text{CO})_2(\text{OH})(\text{N}:\text{NAr})]$ (323).

E. Azido and Nitrene Derivatives

Many reactions between azo, azido, nitro, and isocyanato compounds have been interpreted as proceeding through nitrene intermediates. Organoazides are a convenient source of nitrene radicals, and in the presence of low-valent transition metal systems the generated nitrene may be trapped. Thus, aryl azides (ArN_3 ; $\text{Ar} = \text{Ph}$, *p*- ClC_6H_4 , *p*- $\text{NO}_2\text{C}_6\text{H}_4$, *p*- MeC_6H_4 , *p*- EtC_6H_4) react with $[(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}]_2$ to form arylimino-bridged complexes $[(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}]_2\text{NR}$ (XXV) (155). Alternatively organoazides afford nitrogen complexes rather than nitrenes and have been shown

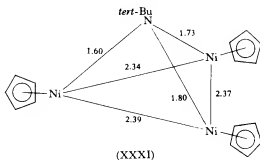
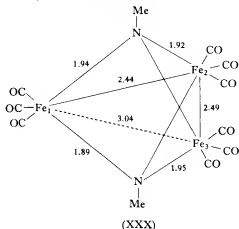


to involve 1,3-dipolar additions to the metal center before elimination of the nitrene in some form (133). Thus the reaction of $[\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}]$ with acid azides, which produces $[\text{Ir}(\text{PPh}_3)_2\text{Cl}(\text{N}_2)]$ and *N*-acyl isocyanate, was thought to involve complex (XXVI) as an intermediate (134, 137, 138). Methyl azide and $[\text{Fe}_2(\text{CO})_9]$, in addition to forming $[\text{Fe}(\text{CO})_5\text{NHMe}]_2$ and $[\text{Fe}_2(\text{CO})_6(\text{MeNCONMe})]$, gave $[\text{Fe}(\text{CO})_3(\text{MeN}_4\text{Me})]$ and $[\text{Fe}_3(\text{CO})_9(\text{NMe})_2]$ (164). An X-ray crystallographic study of the tetraazadiene complex (XXVII) showed the FeN_4 ring system to be approximately planar, with short $\text{N}-\text{N}$ (av. 1.32 Å) and $\text{Fe}-\text{N}$ (av. 1.83 Å) bond lengths,



indicating significant multiple bonding. The bonding representations (XXVIII) and (XXIX) are inconsistent with the near planarity of the ring and the large $M-N'$ distances (174). The compound $\pi-C_5H_5Co(CO)_2$ gave similar air-stable diamagnetic tetraazadiene complexes $[C_5H_5Co(RN_4R)]$ ($R = Ph, Me$), which were inert to strong neutral ligands, but attacked by acids producing N_2 and the corresponding amine. The structure which was favored is represented by (XXVIII) (386), although in the light of the X-ray crystal structure of $Fe(CO)_3(MeN_4Me)$ (174) a related structure is most probable. No well-defined complexes were isolated from the reactions of $EtCOON_3$ with a series of chromium, iron, cobalt, and nickel carbonyl systems (386).

Organonitrogen groups bonding simultaneously three metal atoms occur in $[Fe_3(CO)_9(NMe)_2]$, a product of the reaction of methyl azide and $Fe_2(CO)_9$ (164). An X-ray crystal structure (XXX) showed the $Fe-N$ distances (av. 1.93 Å) to be somewhat shorter than the corresponding



distances for nitrogen bridging two iron atoms, with the Fe—Fe distances somewhat longer. Two of the Fe—Fe distances (2.44 and 2.49 Å) are shorter than the third (3.04 Å), and Fe₁ and Fe₃ are considered not to be bonded (176). Each iron atom obeys the effective atomic number rule. (*tert*-BuN)₂S reacted with $[\pi\text{-C}_5\text{H}_5\text{Ni(CO)}]_2$ to produce a related black paramagnetic (1.68 BM) complex $[(\pi\text{-C}_5\text{H}_5\text{Ni})_3\text{NBu-}i{tert}]$ (XXXI) in which only one alkyimino group bonds to the three nickel atoms (390, 391).

Attempted 1,3-insertion of phenyl azide into the metal-hydride bond of $[\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{H}]$ failed, but at -30°C *p*-tosyl azide gave an unidentified orange powder (325). Hexafluoropropyl azide gave a series of terminal perfluoroalkylimino derivatives in reactions with iridium, rhodium, ruthenium, and osmium carbonyl complexes. R_fN_3 ($\text{R}_f = \text{CF}_3\text{CHFCF}_2-$) reacted with $[(\text{PPh}_3)_2\text{Ir(CO)Cl}]$, $[(\text{PPh}_3)_2\text{Ir(N}_2\text{)Cl}]$, and $[(\text{PPh}_3)_2\text{M(CO)}_3]$ ($\text{M} = \text{Ru, Os}$) (in benzene at ambient temperature) to form $(\text{Ph}_3)_2\text{Ir(CO)Cl(NR}_f)$, $(\text{PPh}_3)_2\text{Ir(NR}_f)\text{Cl}$, and $[(\text{PPh}_3)_2\text{M(CO)}_2(\text{NR}_f)]$ ($\text{M} = \text{Ru, Os}$), respectively (346), thus furnishing examples of the R_fN group adding to and displacing other groups from complexes. $[(\text{PPh}_3)_2\text{Rh(NR}_f)\text{Cl}]$, prepared from $[(\text{PPh}_3)_3\text{RhCl}]$ and R_fN_3 , added carbon monoxide to form $[(\text{PPh}_3)_2\text{Rh(CO)Cl(NR}_f)]$ (346).

Bonding of the R_fN group to the metal was considered to involve nitrogen in a singlet state σ -donating a pair of electrons to the metal, and π -back-donation to an empty *p*-orbital on the nitrogen. The strongly electron withdrawing perfluoroalkyl group enhances the synergic effect, and it was suggested that other predominantly σ -donor ligands bonded to the metal may be essential to enhance the metal's ability to engage in the synergic bonding. Interestingly, $\text{Ru}_3(\text{CO})_{12}$, which contains only strongly π -bonding ligands, reacts with R_fN_3 to give the cluster compound $[\text{Ru}_3(\text{CO})_9(\text{NR}_f)_2]$ (346), analogous to the product (XXX) (176) from $\text{Fe}_2(\text{CO})_9$ and CH_3N_3 (164). *N,N*-Dichloroamines, RNCl_2 ($\text{R} = i{tert}\text{-Bu, C}_6\text{H}_{11}$), reacted with nickel carbonyl in benzene at 0°C to form colorless, water-reactive polymeric materials $[\text{RNCl}_2\text{Ni(CO)}]_n$. Although the nature of these compounds is unclear, an alkylamino group may be present since hydrolysis with water gave the corresponding 1,1'-dialkylurea (80).

F. Azo Derivatives

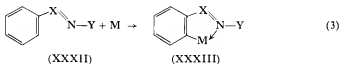
Azo compounds react with metal carbonyls to form derivatives of three types: (1) M—N- and M—C- bonded derivatives resulting from ortho

metallation of a substituent aromatic ring; (2) derivatives which retain the original azo skeleton—the azo compound may π -bond to the metal, insert into metal-hydrogen bonds, or bridge between two metals; (3) *o*-semidine derivatives resulting from the rearrangement of an azo arene.

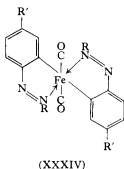
The type of product formed depends on the ring substituents and on reaction conditions (34), and it is convenient here to discuss the various derivatives according to the above types.

1. *Ortho-Metallated Aromatic Azo Derivatives*

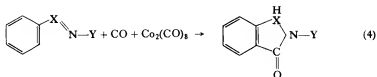
It is well established that many transition metal compounds react with organonitrogen systems of the type $[\text{Ph}-\text{X}=\text{N}Y]$ ($X = \text{RC}$, N , and $Y = \text{alkyl}$, aryl , OH , etc.) with ortho-metallation of the benzene ring according to Eq. (3). For example, azotoluene and azoanisole react with



iron carbonyls to form complexes (XXXIV; $R = \text{CH}_3\text{C}_6\text{H}_4$, $R' = \text{CH}_3$; $R = \text{CH}_3\text{OC}_6\text{H}_4$, $R' = \text{OCH}_3$) (34, 36). Derivatives of the type (XXXIII)

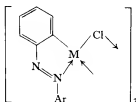


are believed to be important intermediates in the carbonylation and ring-closure reactions of (XXXII) under high carbon monoxide pressure in the presence of carbonylation catalysts such as $\text{Co}_2(\text{CO})_8$ [Eq. (4)]. Rosenthal and Wender have written an authoritative review of the carbonylation of organonitrogen molecules using metal carbonyl catalysts (412), and Parshall



has reviewed the subject of intramolecular aromatic substitution in transition metal complexes including organonitrogen derivatives (398). Brief mention will be made here only of the complexes resulting from these reactions, and those relevant to the mechanisms of the carbonylation and cyclization processes.

Complex (XXXV; $\text{M} = \text{Pd}$) underwent ligand-exchange reactions with $[\text{NaCo}(\text{CO})_4]$ and $[\text{NaM}(\text{CO})_5]$ ($\text{M} = \text{Mn}, \text{Re}$) to form $[\text{ArN}:\text{NC}_6\text{H}_4\text{Co}(\text{CO})_3]$ and $[\text{ArN}:\text{NC}_6\text{H}_4\text{M}(\text{CO})_4]$, respectively. Yellow to red complexes were synthesized with a range of substituents on each benzene ring (254). Similar products of type (XXXIII; $\text{X} = \text{N}, \text{Y} = \text{Ph}$) where $\text{M} = [\text{M}'(\text{CO})_4]$ ($\text{M}' = \text{Mn}, \text{Re}$), $[\text{Mn}(\text{CO})_3\text{PPh}_3]$, $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})]$ ($\text{M} = \text{Fe}, \text{Ru}$),



(XXXV)

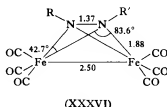
$[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2]$, and $[\pi\text{-C}_5\text{H}_5\text{Ni}]$ were also obtained by the thermal reaction of the corresponding dinuclear carbonyl complexes with azobenzene (98).

Complex (XXXIII; $\text{M} = \text{Ru}(\text{CO})_2$, $\text{X} = \text{N}$, $\text{Y} = \text{Ph}$) reacted with PPh_3 and with *p*-toluidine, with bridge cleavage, and with sodium cyclopentadienide to form $[(\text{azb})\text{Ru}(\text{CO})(\pi\text{-C}_5\text{H}_5)]$. In contrast, TiCl_5 and potassium tris(pyrazolyl)borate gave dicarbonyl complexes $[\pi\text{-C}_5\text{H}_5(\text{azb})\text{Ru}(\text{CO})_2]$ and $[\text{HBpz}_3(\text{azb})\text{Ru}(\text{CO})_2]$, respectively, containing unidentate $\sigma\text{-M}-\text{C}$ -bonded azobenzene (azb) groups (97, 362). Irradiation resulted in evolution of carbon monoxide and chelation of the azobenzene group. $(\text{Ph}_2\text{PCH}_2)_2$ gave $[(\text{Azb})\text{Ru}(\text{CO})_2\text{Cl}(\text{diphos})]$ and 2,2'-bipyridyl gave $[(\text{azb})\text{Ru}(\text{CO})_2(\text{bipy})][(\text{azb})\text{Ru}(\text{CO})_2\text{Cl}_2]$, the first example of a cationic ruthenium carbonyl complex with metal-carbon σ -bonds (97).

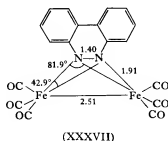
A recent X-ray structural determination of $[(\text{azb})_2\text{Rh}(\text{acetate})]$ provides the first direct confirmation that chelating azoarenes bond through the nitrogen lone pair rather than the $\text{N}-\text{N}$ π -system. The two $\text{Rh}-\text{C}$ bonds are *cis* and the two $\text{Rh}-\text{N}$ bonds are *trans* to one another (157).

2. Derivatives Retaining the Original Azo Skeleton

The compound $[\text{Fe}_2(\text{CO})_6(\text{NMe})_2]$ formed in the reaction of azomethane with $\text{Fe}_2(\text{CO})_9$ was the first example of a binuclear transition metal complex with a bridging methazo group. The $\text{Fe}-\text{Fe}$ bond length (2.50 Å) was found to be long compared with other nitrogen-bridged complexes (Table I), and the $\text{N}-\text{N}$ bond was found to reduce the NFeN and dihedral angles to 42.7° and 58.3° , respectively (XXXVI; $\text{R} = \text{R}' = \text{Me}$) (178).



Related complexes having $\text{N}-\text{N}$ -bonded bridging groups were isolated from the reactions of iron carbonyls with rigid *cis*-azo compounds, such as benzo[*c*]cinnolines (XXXVII) (177), dibenzo-1,4,5-oxadiazepine, 2,3-diazabicyclo[2.2.1]-hept-2-ene, and 4,5,9,10-tetrazapyrene. The latter compound gave a tetranuclear complex $[\text{C}_{12}\text{H}_6\text{N}_4(\text{Fe}(\text{CO})_3)_4]$ presumed to



have $\text{Fe}_2(\text{CO})_6$ units complexed to each azo link (69). 2-(Methylazo)-propene and $\text{Fe}_2(\text{CO})_9$ gave $\{\text{Fe}_2(\text{CO})_6[\text{MeN}:\text{NC}(\text{Me}):\text{CH}_2]\}$ assigned a structure similar to (XXXVI; $\text{R} = \text{CH}_2:\text{CMe}$, $\text{R}' = \text{Me}$) on the basis of

^1H NMR and IR data. Bonding to the metal was considered to be only through the azo group (394). The benzo[*c*]-cinnoline complex (XXXVII) was also obtained using 2,2'-diazidobiphenyl, albeit in small yield, but 2-azidobiphenyl gave $[(o\text{-C}_6\text{H}_5\text{C}_6\text{H}_4\text{N})_2\text{Fe}_2(\text{CO})_6]$ (similar to XXXVI; $\text{R} = \text{R}' = p\text{-PhC}_6\text{H}_4$). If nitrene intermediates are involved in the decompositions of the azido compounds they abstract hydrogen or carbon monoxide in preference to their normal insertion reactions, since the major products contain the urea grouping ($-\text{NHCONH}-$) (115).

Diethylazodicarboxylate ($\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}$) reacted with $[\text{L}_2\text{Ir}(\text{CO})\text{Cl}]$ ($\text{L} = \text{PPh}_3, \text{Ph}_2\text{PMe}$) in benzene solution to form complex (XXXVIII) in which the N—N bond is retained (232). A previous report of the complex (XXXVIII; $\text{L} = \text{PPh}_3$) indicated that it was too unstable for characterization other than by IR spectroscopy (135). ^1H NMR studies of the methyl-diphenylphosphine complex indicate phosphine groups in *trans* positions but there was also evidence for the presence of a second isomer (232), believed to be that with both phosphines in *trans* positions to nitrogen (XXXIX). Isomerism about the N—N bond is possible and although the configurations of the ethoxycarbonyl groups could not be determined for the



(XXXVIII)



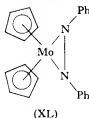
(XXXIX)

trans isomer, they were believed to be in *cis* positions for the complex with *cis*-phosphines (XXXIX). A similar reaction occurred with 4-phenyl-1,2,4-triazoline-3,5-dione to form the related complex $\{(\text{PPh}_3)_2\text{Ir}[(\text{NCO})_2\text{NPh}](\text{CO})\text{Cl}\}$ (232). The bonding of these azo compounds to the metal is believed to be different from that in a classically π -bonded system, and approximate to a σ -bonded rigid three-membered ring model or to a model which essentially retains sp^2 -hybridized nitrogen atoms. The electron-withdrawing substituents lower the energy of the π^* -orbitals to enhance $d\pi-\pi^*$ back-bonding from the metal. The true bonding mode is possibly between these two limiting types (232).

Cleavage of the N—N bond of hexafluoroazomethane by $[\text{Ir}(\text{CO})(\text{PMePh}_2)_2\text{Cl}]$ yielded two isomeric complexes, *cis*- and *trans*- $[\text{Ir}(\text{CO})$

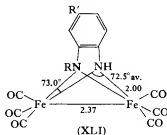
(PMePh₂)₂(NCF₃)Cl]. The *cis* isomer crystallizes directly from the reaction solution with a molecule of benzene of crystallization. Initial formation of the adduct [Ir(CO)(PMePh₂)₂(CF₃NNCF₃)Cl] was suggested, and subsequent weakening and cleavage of the N—N bond was thought to follow as a result of the back-bonding by iridium *d* electrons into the azo-methane π^* -antibonding orbitals (27).

With $[(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2]$, diethylazodicarboxylate inserted into one of the metal-hydrogen bonds to form the yellow complex $(\pi\text{-C}_5\text{H}_5)_2\text{Mo(H)}[\text{N(COOEt)N(H)COOEt}]$. Azodiisobutyronitrile $[\text{NCMe}_2\text{CN:NCMe}_2\text{CN}]$ reacted with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ to form $[\text{Rh}(\text{CO})_2\text{Cl}]_2[\text{NCCMe}_2\text{N:NCMe}_2\text{CN}]$ in which the chlorine bridges have been replaced by the azo compound, bridging through the nitrogen atoms of the cyanide groups (457). In contrast, azobenzene substitutes both hydrido groups of $[(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2]$ in boiling toluene or THF to form the deep red, air-sensitive complex $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo(PhNNPh)}]$, assigned structure (XL) on the basis of IR and ¹H NMR data, and the lack of reactivity towards $\text{Ph}_2\text{P(CH}_2)_2\text{PPh}_2$. The tungsten compound failed to react (387).

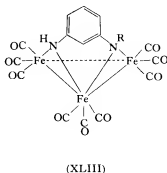
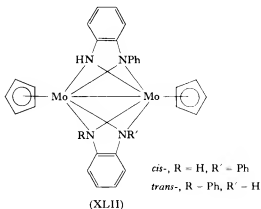


3. *ortho*-Semidine Derivatives

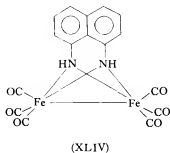
Azobenzenes reacted with iron carbonyls to give the complexes $[(\text{R}'\text{C}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4\text{R}')\text{Fe}_2(\text{CO})_6]$ ($\text{R}' = \text{H}, p\text{-Me}, p\text{-MeO}$) for which structures containing the original azobenzene skeleton were postulated (36).



However, a later X-ray structure of the azobenzene complex showed the ligand to have rearranged to the *o*-semidine group shown in (XLI; $R = \text{Ph}$, $R' = \text{H}$). The small FeNFe angles (71.9 and 73.2°) related to the small $\text{Fe}-\text{Fe}$ distances were thought to be significant since they supported the view that the nature and number of bridging groups determine the metal separation (39). This conclusion has now been challenged (42). A double *o*-semidine bridge was postulated for $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{PhNC}_6\text{H}_4\text{NH})]_2$ (XLI), a product of the reaction of $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ with azobenzene (98). The trinuclear complex (XLIII), formulated with nitrogen atoms bridging

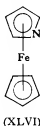
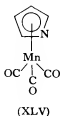


different pairs of metal atoms, was the second product from the reaction of *p*-azotoluene with iron carbonyls (34). The mechanism by which these remarkable rearrangements occur is not yet understood. The related complex (XLIV) was obtained in a small yield from the reaction of 1,8-diazidonaphthalene or 1-amino-8-azidonaphthalene with $\text{Fe}_2(\text{CO})_9$ (115).



G. π -Bonded Heterocyclic Derivatives

The first π -bonded azacyclic derivative $[(\pi\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_3]$ (XLV) was produced from the reaction of pyrrole with $[\text{Mn}_2(\text{CO})_{10}]$ in light petroleum or diglyme at 130°C . Pyrazoles and triazoles were found to form related complexes (288). An alternative route to (XLV) was the reaction of the potassium salt of the pyrrole with $[\text{Mn}(\text{CO})_5\text{Br}]$, a route used to synthesize mono-, di-, and tetramethyl-substituted pyrrole derivatives (120, 132, 289). With $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}]$ the potassium salts in refluxing benzene gave azaferrocene (XLVI) (289), which was prepared also in small yield by the reaction of ferrous chloride with a mixture of NaC_3H_5 and $\text{NaC}_4\text{H}_4\text{N}$ (306). Optical isomers of $[(\text{MeC}_4\text{H}_3\text{N})\text{Fe}(\text{C}_3\text{H}_5)]$ were resolved, and the absolute configuration of the forms determined (44, 415). Intermediate σ -pyrrole complexes (see Section II,A,1) analogous to $[\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_2]$



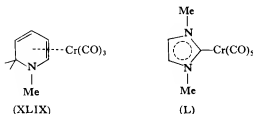
$\text{CH}_2\text{CH}=\text{CH}]$ (for example), were isolated under mild reaction conditions, and on heating gave π -complexes (400). Pauson *et al.* extended the potassium pyrrolide route to the preparation of $[\text{Mn}(\text{CO})_3(\text{heterocycle})]$ (heterocycle = XLVII; $\text{R} = \text{Me}$, $\text{R}'' = \text{acyl}$; $\text{R} = \text{R}' = \text{Me}$, $\text{R}'' = \text{acyl}$: 2-methylindole, and 1,2,3,4-tetrahydrocarbazole) but found that indoylpotassium gave a product $[\text{C}_9\text{H}_8\text{Mn}(\text{CO})_3]$ from which the nitrogen had been abstracted (401). Irradiation of $[(\pi\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_3]$ with MPh_3 ($\text{M} = \text{P}$, As , Sb) in hexane solution gave the simple substitution products $[(\pi\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_2(\text{MPh}_3)]$. However, no cationic nitrosyl complex of the type $[(\pi\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_2\text{NO}]^+$ could be synthesized by replacing carbon monoxide with nitric oxide. With acetylenes only decomposition of the starting material was achieved (311). ^1H NMR measurements have proved valuable in assigning π - or σ -bonding to the heterocyclic ring. In general, the signals are shifted upfield for both σ - and π -bonded pyrrole groups, but the chemical shift difference between α - and β -protons for *N*-pyrrole complexes is signifi-

cantly reduced compared to pyrrole itself, and splittings between them are more complex. The opposite was found for π -complexes (400, 401). ^{55}Mn NQR studies of $[(\pi\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_3]$ suggest that the π -pyrrolenyl—Mn bonding is significantly distorted such that the Mn—N and Mn— αC bond distances are shorter than Mn— βC . The bonding was considered to be more correctly described as a metal heterocyclic allylic system donating four electrons and an olefin bond donating two electrons to the metal, rather than a six-electron $\pi\text{-C}_5\text{H}_5^-$ -type bond (XLVIII) (195).



(XLVIII)

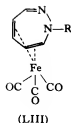
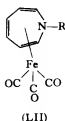
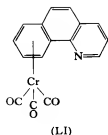
Pyrolysis of *N*-methylpyridinium iodo- and hydridopentacarbonyl chromium in a high vacuum (130°C) afforded small yields of a red-orange, diamagnetic volatile π -complex (XLIX) in which the nonaromatic delocalized π -system donates six-electrons to the metal. Originally formulated as $[(\pi\text{-C-MeC}_5\text{H}_4\text{N})\text{Cr}(\text{CO})_3]$, migration of the methyl group from nitrogen to possibly the α -position was thought to accompany the elimination of HI (207, 208, 208a). The 1,3-dimethyl imidazolium compound on heating to 120°C produced the carbene complex (L) and hydrogen (383, 384a).



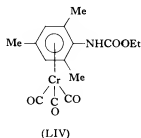
(XLIX)

(L)

Attempts to prepare chromium and iron carbonyl π -complexes from a series of mixed condensed ring systems were successful, although the metals were bonded not to the heterocyclic but to the carbocyclic ring systems (LI) (45, 201, 378). *N*-Ethoxycarbonylazepine and diazepine react with iron carbonyls to form $[\text{Fe}(\text{CO})_3(\text{C}_6\text{H}_6\text{NCO}_2\text{Et})]$ (LII; $\text{R} = \text{COOEt}$)



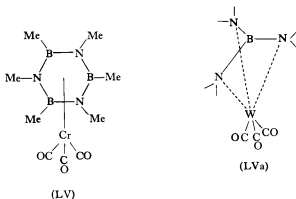
and $[\text{Fe}(\text{CO})_3(\text{C}_5\text{H}_5\text{N}_2\text{CO}_2\text{Et})]$ (LIII; $\text{R} = \text{COOEt}$), respectively, in which only two of the ring double bonds are bonded to the metal (210, 399, 430). Tautomeric changes were detected for (LII) by ^1H NMR studies, but shown to be less important for ring-substituted acyl derivatives (225, 245). Treatment of the product with NaOMe in methanol cleaves the ethoxycarbonyl group to yield the simple azepine derivative $[\text{Fe}(\text{CO})_3(\text{C}_6\text{H}_6\text{NH})]$ (LII; $\text{R} = \text{H}$). Similar complexes were formed with 2,4,6-trimethylazepine and the *N*-ethoxycarbonyl derivative (210). With $\text{Cr}(\text{CO})_6$, *N*-ethoxycarbonylazepine suffered extrusion of the ring nitrogen to give $[\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3]$, whereas the trimethyl derivative underwent contraction of the seven-membered ring to form (LIV) (210). Attempts to form π -complexes from



fluorinated nitrogen heterocyclic π -systems have resulted only in displacement of fluorine and formation of metal-carbon σ -bonds (84, 85, 99, 100, 152, 153, 233).

Brown made a theoretical study of the electronic structure of π -complexes of heteroaromatic systems, and predicted π -complexes of borazoles to be less stable than the corresponding complexes of benzene (95). Although many attempts to synthesize a π -borazole complex were unsuccessful, $\text{Et}_3\text{B}_3\text{N}_3\text{Me}_3$ and $\text{Me}_3\text{B}_3\text{N}_3\text{Et}_3$ derivatives were later prepared from the hexacarbonyl by irradiation. $[\text{Cr}(\text{CO})_3(\text{Me}_6\text{B}_3\text{N}_3)]$ (LV) was eventually

synthesized thermally from $[(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3]$ and hexamethylborazole (406, 464), and $[\text{Et}_3\text{B}_3\text{N}_3\text{Me}_3]$ and $[\text{Me}_3\text{B}_3\text{N}_3\text{Et}_3]$ by irradiation of the hexacarbonyl (163). An eclipsed configuration with the nitrogen in trans positions to π -acidic carbonyl groups was predicted, with ring chromium



bonding more localized than in $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ (234). Substitution reactions with phosphines, phosphites, MeCN, and dioxane occurred under surprisingly mild conditions (E_a 5.9–10.9 kcal/mole for phosphites) with cleavage of the metal–ring bonds. A second-order rate law was found, indicating a primary rate-determining attack of the ligand at either the metal or ring ligand (162). In complex (LVa) the triaminoborane occupies three coordination position and functions as a π -acceptor ligand with a relatively strong W–B interaction (416a). Metal–B–N π -bonding was also postulated for the complexes $[\text{Fe}(\text{CO})_3(\text{Me}_2\text{NB}(\text{Me})\text{NMe}_2)]$ and $[\text{Fe}(\text{CO})_3(\text{CH}_2=\text{CHB}(\text{Br})\text{NMe}_2)]$ (416b).

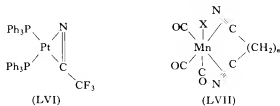
H. Nitrile Complexes

Nitrile derivatives of the metal carbonyls have been discussed together with other nitrogen donor molecules in a number of contexts. Much of the early work has been reviewed by Manuel (337) in his article on Lewis base–metal carbonyl complexes in Volume 3 of this series, and by Strohmeier (436) in his review of photochemical substitution reactions. In general, nitriles are weaker Lewis donors than phosphorus and nitrogen bases (436), but compared to carbon monoxide, better electron donors but poorer acceptors (427). Force constants and assignments for a series of complexes $[(\text{MeCN})_x\text{M}(\text{CO})_{6-x}]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) were studied (165, 228, 296) and

acetonitrile shown to possess a small but real ability to accept π -electrons in competition with carbon monoxide (431). The contribution to the bonding from the resonance form $[\text{C}^-\text{N}^+\text{M}]$ was estimated to be $\sim 5\%$ (145). π -Acceptor strengths of ligands L in complexes $[\text{AreneCr}(\text{CO})_2\text{L}]$ were placed in the order nitrile $<$ isonitrile $\sim \text{PR}_3 < \text{CO}$ and the stability of the derivative in the order $\text{L} = \text{CO} > \text{PR}_3 > \text{NR}_3 > \text{nitrile} > \text{oxygen compound}$ (436). From dipole moment studies on $[\text{AreneCr}(\text{CO})_2\text{L}]$ ($\text{L} = \text{nitrile}$, isonitrile, N bases) it was concluded that the polarity of the σ -bond was primarily responsible for the stability of the $\text{Cr}-\text{X}$ bond, and that π -bonding only adds a secondary bond strengthening (432). Moments of σ -bonds in nitrile and isonitrile derivatives were found to be smaller than in tertiary nitrogen and phosphorus derivatives, in agreement with the lower stability of these complexes (435).

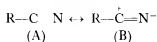
Nitrile complexes may be synthesized by the thermal reaction of the parent carbonyl with the appropriate nitrile, but elevated temperatures are required, and this often leads to complications of thermal decomposition and/or further reaction. A more controlled route widely used is the irradiation of the metal carbonyl in a solution of the nitrile, or in a donor solvent capable of forming a labile complex such as $\text{Cr}(\text{CO})_5$, THF. Addition of the nitrile displaces the weakly bound solvent molecule (172, 248).

Nitriles are known to bond to transition metals either through the nitrogen lone pair of electrons, or through the $\text{C}\equiv\text{N}$ π -system. The former is the most usual and is found for the common nitriles bonded to transition metals in low and normal oxidation states (385, 460). π -Bonded nitrile groups have been detected when the substituent group is extremely electron withdrawing or when the geometry of the molecule does not allow nitrogen lone pair donation (72, 189, 192). Trifluoroacetonitrile reacted with $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{trans-stilbene})]$ to form $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{NCCF}_3)]$, formulated (LVI) with a three-membered ring system to indicate that the main interaction between the metal and the ligand is extensive $d\pi-\pi^*$ bonding arising from the π -acceptor properties of the nitrile (72). Dinitriles in which the functional



groups are separated by up to three carbon atoms form the complexes $[M(CO)_3X(NC-R-CN)]$ [$M = Mn, Re$; $X = Cl, Br$; $R = (CH_2)_n$, $n = 1, 2, 3$, or $o-C_6H_4$] (LVII) in which the linearity of the $C-C-N$ units restricts the bonding to the metal to π -type. Such complexes were unstable to thermal decomposition, and the bidentate ligand was displaced readily with nitrogen and phosphorus chelates (189, 192).

Bonding of a nitrile to an electron acceptor through the lone pair in general increases ν_{CN} (427, 460), although examples, such as $CoH(RCN)(PPh_3)_3$ (351), have been cited for which ν_{CN} decreases $\sim 50\text{ cm}^{-1}$ (128, 218). Two schools of thought exist to explain the general increase in ν_{CN} . In one the free nitrile is considered to have a bond order approximately intermediate between 2 and 3 because of mesomerism (145, 184, 224):



On complexing, the contribution of (A) to the bonding is increased, since only the linear form $R-C \equiv \overset{+}{N}-M^-$ and not the bent form $R-\overset{+}{C}=N^-$ is found in complexes. The bond order and ν_{CN} are thus expected to increase (224). Alternatively the shift to higher frequencies may be due to the predominance of a kinematic effect (407, 443). For acetonitrile, bonding to BF_3 caused ν_{CN} to increase by $\sim 125\text{ cm}^{-1}$ (130, 441) but in complexes of the type $[(MeCN)M(CO)_3]$ ($M = Cr, W$) smaller increases of $20\text{--}50\text{ cm}^{-1}$ were found (413, 443).

Acrylonitrile has the additional possibility of bonding through the olefinic π -system, which is the preferred mode for metals with large d^n configurations and in complexes having extensive π -bonding. Thus one form of $[Fe(CO)_4(CH_2=CHCN)]$ (297), $[\pi-C_5H_5Mn(CO)_2CH_2:CHCN]$ (469), and $[W(CO)_3(CH_2=CHCN)_1]$ (413, 443) have olefinic-bonded groups, while $[Mn_2(CO)_9(CH_2:CHCN)]$ (471), and $[W(CO)_4(CH_2=CHCN)_2]$ (413, 443) have nitrogen-bonded groups. Coordination through the nitrogen causes ν_{CN} to increase in general, although only to a small extent; ν_{C-C} remains very little changed and occurs at $\sim 1600\text{ cm}^{-1}$. Bonding through the π -olefinic system causes a small decrease in ν_{CN} of up to 25 cm^{-1} (413, 469), but lowers ν_{C-C} from 1610 cm^{-1} for the free ligand to $\sim 1450\text{ cm}^{-1}$ in complexes (413). 1H NMR measurements provide perhaps the most conclusive indication of π -type bonding since large (~ 3.7 ppm) upfield shifts were observed for the ABC pattern of the olefinic

protons compared with the free ligand (413, 443, 469). The ^1H NMR spectrum for nitrogen-bonded acrylonitrile groups differs little from that of the free ligand (339).

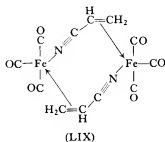
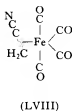
Nitriles bonded through the $\text{C}\equiv\text{N}$ π -system exhibit characteristically large decreases in ν_{CN} compared with the free ligands (189, 192). For $[\text{Et}_2\text{NCH}_2\text{CN}]$, coordinating through both the amino group and $\text{C}\equiv\text{N}$ π -system, decreases of $\sim 100\text{ cm}^{-1}$ were observed (276), whereas for dinitriles of the type $[\text{NC}(\text{CH}_2)_n\text{CN}]$ decreases of up to 230 cm^{-1} were detected (192).

The relative lability of nitrile complexes compared to similar complexes with aromatic amine and phosphine ligands renders them useful catalysts (433) and starting materials for other substituted carbonyl complexes. Thus $[\text{M}(\text{CO})_3(\text{MeCN})_3]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) have been used extensively as sources of $\text{M}(\text{CO})_3$ (68, 201, 219, 290, 296, 305, 312, 314, 444), and even $\text{M}(\text{CO})_4$ moieties (200, 305).

1. Nitriloolefin Complexes

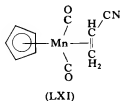
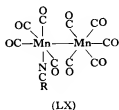
Derivatives of tetracyanoethylene have been reviewed (29, 408) and are omitted from this survey.

The thermal or photolytic reaction of $\text{Fe}_2(\text{CO})_9$ with acrylonitrile yields the yellow volatile substitution complex $[\text{CH}_2:\text{CHCNFe}(\text{CO})_4]$ (297), in which the nitrile was shown to bond through the π -system (LVIII). The $\text{C}=\text{C}$ bond was extended from 1.339 \AA for gaseous acrylonitrile to 1.40 \AA in the complex (331). The ν_{CN} was observed at a slightly lower frequency than for the uncomplexed nitrile, in keeping with a group not bonded to the metal (297). The isomeric nitrile-bonded product was obtained from $\text{Fe}(\text{CO})_5$, but in addition a dinuclear complex $[\text{Fe}(\text{CO})_3(\text{CH}_2:\text{CHCN})]_2$ was produced in which the iron atoms are bridged by nonlinear acrylonitrile groups bonding via both nitrogen and the $\text{C}=\text{C}$ π -system (LIX) (420, 470).



When this reaction was performed in caustic potash solution a viscous yellow oil was formed, which when treated with acetone/ether gave the anionic complex $[\text{NCCH}_2\text{CH}_2\text{Fe}(\text{CO})_3]^-$. Hydrocyanic acid treatment gave the hydride complex $[\text{NCCH}_2\text{CH}_2\text{Fe}(\text{CO})_3\text{H}]$, methyl acrylate gave the methoxy carbonyl complex $[\text{MeO}_2\text{CFe}(\text{CO})_3\text{CH}_2\text{CH}_2\text{CN}]$, while $[\text{NCCH}_2\text{CH}_2\text{Cl}]$ gave the dicyanoethyl complex $[\text{Fe}(\text{CO})_3(\text{CH}_2\text{CH}_2\text{CN})_2]$. The nature of these complexes has not been established (121). Cleavage of the halogen bridge in $\{[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{Br}\}\text{BF}_4$ was achieved with acrylonitrile and MeCN to produce the N-bonded derivatives $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{NCR}]\text{BF}_4$ ($\text{R} = \text{CH}:\text{CH}_2, \text{CH}_3$) (205, 206).

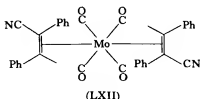
Irradiation of acrylonitrile and $[\text{Mn}_2(\text{CO})_{10}]$ gave the nitrile-bonded derivative $[\text{Mn}_2(\text{CO})_9\text{NCCH}:\text{CH}_2]$, assigned structure (LX), with the nitrile in an equatorial position, in contrast to the axial structure of $[\text{Mn}_2(\text{CO})_9\text{PPh}_3]$. The different structures were believed to be related to the stronger tendency of PPh_3 compared with the nitrile to π -bond to the metal (471). The comparable reaction with $[\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3]$ gave $[\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{CH}_2=\text{CHCN})]$ in which the acrylonitrile bonds through the $\text{C}=\text{C}$ π -system (LXI) (469).



Acrylonitrile and related compounds displace all the carbonyl groups from nickel carbonyl to form $[(\text{RCH}:\text{CHCN})_2\text{Ni}]$, in which the nitrile bonds through the olefinic double bond (222, 418). The bis(acrylonitrile) complex catalyzes many reactions, including the conversion of acrylonitrile and acetylene to heptatrienenitrile and the polymerization of acetylene to cyclooctatetraene (418). Cobalt carbonyl gave a brown-red amorphous material with acrylonitrile, which had ν_{CN} absorptions typical of uncoordinated nitrile groups, but interestingly, the presence of $\text{C}\equiv\text{N}$ groups was also indicated (419). In acidic methanol, cobalt carbonyl converts α,β -unsaturated nitriles to saturated aldehydes (459).

Acrylonitrile complexes of three types are known for Cr, Mo, and W carbonyls, $[(\text{CH}_2\text{CHCN})_x\text{M}(\text{CO})_{6-x}]$ ($x = 1, 2, 3$), and are prepared by

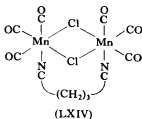
thermal or photolytic reactions from the parent carbonyls, or alternatively by displacement of other ligands. For ($x = 1, 2$; $M = Cr, W$), complexes were assigned N-bonded groups on account of the observed high frequency of ν_{CN} and constant position of $\nu_{C=C}$ (191, 250, 339, 413, 443). The mono-substituted products of chromium and molybdenum were found to be less stable than the tungsten analog, and are normally prepared from the corresponding acetonitrile complexes (413). Thermal reactions of acetonitrile and the hexacarbonyls led to $[(CH_2:CHCN)_2M(CO)_2]$ ($M = Cr, Mo$), believed to be polymeric because of their insolubility in organic solvents; but since ν_{CN} was slightly lower than that for the free nitrile, bridging via the nitrogen lone pair was thought unlikely (340). This reaction in the presence of PPh_3 gave $[Mo(CH_2:CHCN)(CO)_3(PPh_3)_2]$ (161). $[PhCH:C(Ph)CN]$ gave the red complex $\{[PhCH:C(Ph)CN]_2Mo(CO)_4\}$ (LXII), believed to have olefinic type linkages as a result of a lowering of



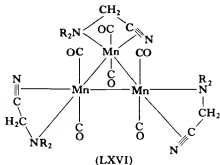
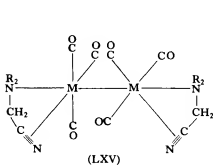
the energy of the lowest unoccupied orbitals brought about by the presence of phenyl substituents (419). Similar attachment occurs for *trans*- $[(CH_2:CHCN)_3M(CO)_3]$ ($M = Mo, W$) since both ν_{CN} and $\nu_{C=C}$ occur at low energy ($\Delta\nu_{CN} \sim 10 \text{ cm}^{-1}$, $\Delta\nu_{C=C} \sim 160 \text{ cm}^{-1}$) (413, 443). Interestingly, these *trans* complexes were prepared from the corresponding *cis*-acetonitrile complexes, and isomerization was interpreted in terms of the relative *trans*-directing ability of the ligands (443). Treatment of $[\pi\text{-ArCr(CO)}_3]$ ($Ar = C_6H_6$, 1,4-($MeCO_2$) $_2C_6H_4$, 1,3,5- $Me_3C_6H_3$, Me_6C_6) with acrylonitrile gave $[ArCr(CO)_2CH_2:CHCN]$. When $Ar = C_6H_6$, Me_6C_6 , and $Me_3C_6H_3$ bonding through the olefinic system occurs, whereas for $Ar = (CH_3CO_2)C_6H_5$ the nitrogen lone pair bonds to the metal. Thus electron-withdrawing substituents on the ring favor the bonding through nitrogen (250). $[IrH(CO)(PPh_3)_2(NCCH:CHR)]$ (LXIII; $R = H, CN$) were obtained from heating $[IrH(CO)(PPh_3)_3]$ and the nitrile. Substitution of PPh_3 occurs in preference to insertion into the metal-hydrogen bond (31).

2. π -Nitrile Derivatives

Dinitriles of the type $[\text{NC}(\text{CH}_2)_n\text{CN}]$ with carbon chains too short to permit σ -bonding to the same metal through both nitrogen lone pairs were found to π -bond in preference to bridge between two metal moieties. The complexes $[\text{M}(\text{CO})_3(\text{NCRCN})\text{X}]$ [$\text{M} = \text{Mn}, \text{Re}$; $\text{R} = (\text{CH}_2)_n$ where $n = 1, 2, 3$, or $o\text{-C}_6\text{H}_4$; $\text{X} = \text{Cl}, \text{Br}$] (LVII) were isolated as relatively thermal and air-stable complexes, which reacted with other donor molecules (MeCN , bipy , diphos) with displacement of the dinitrile. All the dinitrile complexes exhibited three ν_{CO} , consistent with *fac* structures (LVII) and low $\text{C}=\text{N}$ stretching frequencies ($2041\text{--}2072\text{ cm}^{-1}$) arising from π -bonded nitrile groups (192). Structural isomers $[\text{M}(\text{CO})_3(\text{NCRCN})\text{X}]$, which are dimeric through halogen bridges and contain dinitrile ligands bonding through one nitrogen atom, were prepared by the same route as Farona *et al.*, the products depending critically on the reaction conditions (179a). In addition the dinuclear manganese complex $\{\text{Mn}_2(\text{CO})_6[\text{NC}(\text{CH}_2)_3\text{CN}]\text{Cl}_2\}$ was isolated and shown by IR spectroscopy to contain two bridging chlorines and a bridging N-bonded dinitrile (LXIV) (192).



The thermal reactions of $[\text{Et}_2\text{NCH}_2\text{CN}]$ with chromium, molybdenum, tungsten, manganese, and iron carbonyls gave complexes of the type



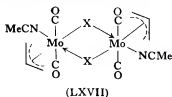
$[\text{M}(\text{CO})_3(\text{Et}_2\text{NCH}_2\text{CN})]_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), $[\text{Mn}(\text{CO})_2(\text{Et}_2\text{NCH}_2\text{CN})]_3$, and $[\text{Fe}(\text{CO})_3(\text{Et}_2\text{NCH}_2\text{CN})]$, in which the nitrogen ligand acts as a bidentate four-electron donor through the amine nitrogen atom and the $\text{C}\equiv\text{N}$ π -system. On the basis of the IR spectra, structures (LXV) and (LXVI) were proposed for the polynuclear systems, decreases of $\sim 100\text{ cm}^{-1}$ being observed for $\nu_{\text{C}\equiv\text{N}}$ on coordination. Cleavage of the metal-metal bond in $[\text{M}(\text{CO})_3(\text{Et}_2\text{NCH}_2\text{CN})]_2$ ($\text{M} = \text{Cr}, \text{W}$) was achieved using sodium and iodine to form $\text{Na}[\text{Cr}(\text{CO})_3(\text{R}_2\text{NCH}_2\text{CN})]$ and $[\text{W}(\text{CO})_3(\text{R}_2\text{NCH}_2\text{CN})]\text{I}$. Weak paramagnetism was detected for some of the complexes (276).

3. σ -Nitrile Complexes

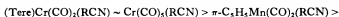
The substitution products $[\text{M}(\text{CO})_{6-x}(\text{NCR})_x]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $x = 1, 2, 3$; $\text{R} = \text{Me}$) are all known, although $[(\text{MeCN})\text{Mo}(\text{CO})_5]$ is extremely unstable, compared with its tungsten and chromium analogs (145, 165, 172, 191, 250, 413, 427, 428, 437, 439, 440, 442). Other nitriles give similar complexes but have been less studied (173, 437). The fluorinated nitrile $\text{C}_6\text{F}_5\text{CN}$ forms the complexes $[(\text{C}_6\text{F}_5\text{CN})\text{M}(\text{CO})_5]$ and *cis*- $[(\text{C}_6\text{F}_5\text{CN})_2\text{M}(\text{CO})_4]$ which were too unstable to be isolated but which were found to be very similar to those of nonfluorinated nitrile derivatives (409). Mixed ligand complexes of the type $[\text{M}(\text{CO})_3(\text{RCN})\text{L}_2]$ are also known (409a). The ready displacement of acetonitrile from the air-sensitive complexes has been mentioned previously, and acetylenes and olefins were found to undertake the displacement under mild conditions (312, 313). However $[\text{CF}_3\text{C}\equiv\text{CCF}_3]$ reacts with $[\text{M}(\text{CO})_3(\text{MeCN})_3]$ ($\text{M} = \text{Mo}, \text{W}$) to produce the seven-coordinate complexes $[(\text{CF}_3\text{C}_2\text{CF}_3)_3\text{M}(\text{NCMe})]$ ($\text{M} = \text{Mo}, \text{W}$), whereas by contrast, $[\text{RC}\equiv\text{CR}]$ ($\text{R} = \text{Et}, \text{Ph}$) gave the corresponding carbonyl complex $(\text{RC}_2\text{R})_3\text{W}(\text{CO})$ (305, 314). Treatment of the carbene complexes $[\text{L}(\text{CO})_4\text{MC}(\text{OMe})\text{Me}]$ ($\text{M} = \text{Cr}, \text{L} = \text{CO}$; $\text{M} = \text{W}, \text{L} = \text{PPh}_3$) and $[\text{Mn}_2(\text{CO})_9\text{C}(\text{OMe})\text{Me}]$ with dimethylhydrazine gave *cis*- $[(\text{CO})_4\text{W}(\text{NCMe})\text{L}]$ (198, 199) and equatorial- $[\text{Mn}_2(\text{CO})_9(\text{NCMe})]$, respectively (209). The complexes of the latter type were also formed by irradiation of $[\text{Mn}_2(\text{CO})_{10}]$ with RCN ($\text{R} = \text{Me}, \text{Ph}$) (471).

The oxidative-displacement reaction of allyl compounds RX ($\text{R} = \text{C}_3\text{H}_5, \text{C}_4\text{H}_7, \text{C}_3\text{H}_4\text{Cl}$; $\text{X} = \text{I}, \text{SCN}$) with $[(\text{MeCN})_3\text{M}(\text{CO})_3]$ ($\text{M} = \text{Mo}, \text{W}$) gave the metal(II) complexes $[(\text{MeCN})_2\text{M}(\text{CO})_2(\pi\text{-allyl})\text{X}]$, which reacted further with bipy, *o*-phen, diacetylbis(dimethylhydrazone), and C_5H_5^- to displace the remaining nitrile groups (170, 253), and with PPh_3 to form

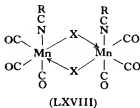
$[\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{MeCN})_2]$ and $[\text{Mo}(\text{CO})_3(\text{MeCN})(\text{PPh}_3)_2]$ (171). One nitrile group was displaced on heating the allyl-nitrile complex, with the formation of $[(\text{MeCN})\text{Mo}(\text{CO})_2(\pi\text{-allyl})\text{X}]_2$ (LXVII) (170). PhCN



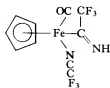
replaced acetonitrile from (LXVII), whereas PPh_3 reacted with the corresponding bridged-halogen complexes to form $[\text{Mo}_2(\text{CO})_4(\text{PPh}_3)_{6-n}(\text{MeCN})_n]$, which were not fully characterized (170). Cationic complexes of the type $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2(\text{MeCN})_2]^+$ ($\text{M} = \text{Mo}, \text{W}$) and $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})(\text{MeCN})(\text{PPh}_3)_2]^+$ were prepared from $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{Cl}]$ and $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})(\text{PPh}_3)_2\text{Cl}]$, respectively, in the presence of a halogen acceptor (AlCl_3) (446), and irradiation of $[\text{ArCr}(\text{CO})_3]$ [$\text{Ar} = 1,4\text{-(MeCO}_2)_2\text{C}_6\text{H}_4$; $1,2\text{-(MeO}_2\text{C)}_2\text{C}_6\text{H}_4$; $1,3,5\text{-Me}_3\text{C}_6\text{H}_3$; Me_6C_6] with PhCN or MeCN gave the complexes $[\text{ArCr}(\text{CO})_2(\text{RCN})]$. The following sequence of decreasing acceptor strength was deduced from differences in stability of the corresponding nitrile complexes (258, 259, 469; 432, 434, 438):



Nitrile complexes of manganese and rhenium were synthesized by the direct reaction of the nitrile with the binary carbonyls or halides (429), and also by displacement of dinitriles from the complexes $[\text{M}(\text{CO})_3(\text{NCRN})\text{Br}]$ [$\text{R} = (\text{CH}_2)_n$, $n = 1, 2, 3$; C_6H_4] (192). Complexes of the types $[\text{M}(\text{CO})_3\text{NCMe}]\text{PF}_6$ ($\text{M} = \text{Mn}, \text{Re}$) (140), $[\text{M}(\text{CO})_3(\text{RCN})_2\text{X}]$ ($\text{M} = \text{Mn}, \text{Re}$, $\text{X} = \text{Br}$, $\text{R} = \text{Me}, \text{Ph}$ (429); $\text{M} = \text{Mn}$, $\text{X} = \text{Cl}, \text{Br}$, $\text{R} = \text{Me}$) (192), *cis*- $[\text{Re}(\text{CO})_4(\text{MeCN})\text{Br}]$, and $[\text{Mn}(\text{CO})_3(\text{RCN})\text{X}]_2$ ($\text{R} = \text{Me}$, $\text{X} = \text{Cl}$ (192); $\text{R} = \text{CH}_2\text{:CH}$, $\text{X} = \text{Br}$) (429) (LXVIII) have been prepared, the



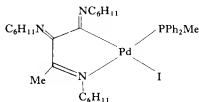
nitriles bonding through the nitrogen in all complexes. The compounds $[M(CO)_3(PhCN)_2Br]$ ($M = Re, Mn$) were found to dissociate in chloroform but not dimethyl sulfoxide solution (429). The carbonyl halide derivatives $[Ru(CO)_2(RCN)_2Cl_2]$ ($R = Me, Ph$) were reported (224a) and treatment of $\{[\pi-C_5H_5Fe(CO)_2]Cl\}^+BF_4^-$ with methyl cyanide gives $[\pi-C_5H_5Fe(CO)_2NCMe]BF_4$ (205, 206). Reaction of CF_3CN under pressure with $[\pi-C_5H_5Fe(CO)_2CH_3]$ gave an acetimino derivative, $[CF_3C:N(H)Fe(CO)(NCCF_3)-\pi-C_5H_5]$ (LXIX) through abstraction of a proton. The strong π -electron acceptor properties of CF_3CN are indicated by the high value of ν_{CO} , but



(LXIX)



(LXX)



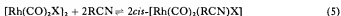
(LXXa)

the acetimino group was considered to have poor π -acceptor properties because of the unfavorable resonance forms:



Phosphorus ligands $[PPh_3, P(OPh)_3]$ displace carbon monoxide and cause a lowering of ν_{CN} by $\sim 70\text{ cm}^{-1}$ through increased $d\pi-\pi^*$ bonding with the CN group (315). Related groups $[-C(R^1)=NR]$ result from the insertion of isonitriles into metal-alkyl bonds, but for the reaction of $C_6H_{11}NC$ with *trans*- $[MePdI(PPh_2Me)_2]$ at 0°C up to three successive insertion processes

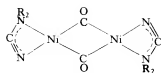
occurred to form (LXXa) (468). Protonation of $[(\pi\text{-C}_5\text{H}_5\text{Fe})_2(\text{CO})_3(\text{CNMe})]$ with aqueous HCl gave $[(\pi\text{-C}_5\text{H}_5\text{Fe})_2(\text{CO})_3(\text{CNHMe})]^+$, which contains the isomeric type of group $>\text{C}=\text{NHMe}$ which acts as a bridging unit (447). CF_3COCN reacted with $[\text{Ir}(\text{PPh}_2)_2(\text{CO})\text{Cl}]$ ($\text{R} = \text{Ph}, \text{Me}$) to form $[\text{Ir}(\text{CO})(\text{PPh}_2)_2\text{Cl}(\text{CF}_3\text{COCN})]$, assigned the Ir(III) structure (LXX), in which the cyano group is not involved in bonding to the metal (230). The cyanomethyl group, $-\text{CH}_2\text{CN}$, acts only as a one-electron donor in the complexes $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{LCH}_2\text{CN}]$ and $[\text{Fe}(\text{CO})_2(\text{NO})\text{L}(\text{CH}_2\text{CN})]$ ($\text{L} = \text{CO}, \text{PPh}_3$) (26, 123). Of interest are the reactions of the cyanomethylene group, generated from diazoacetonitrile with palladium chloride compounds, for which insertion into metal-chlorine bonds occurs (341). Cleavage of the halogen bridge in $[\text{Rh}(\text{CO})_2\text{X}]_2$ ($\text{X} = \text{Cl}, \text{Br}$) was achieved with a series of alkyl and aryl nitriles to form *cis*- $[\text{Rh}(\text{CO})_2(\text{RCN})\text{X}]$. Aromatic nitrile derivatives were more stable than aliphatic derivatives, MeCN and EtCN derivatives being isolated only at -78°C . Two forms of the complexes were detected, the normal square-planar complex and a form thought to have metal-metal interactions in the solid state (453, 454). In solution, the equilibrium (5) was shown by IR spectroscopy to be dependent on the basicity of the nitrile (454).



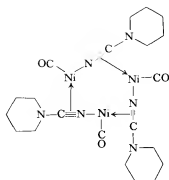
Carbonylate salts of cobalt, iron, ruthenium, manganese, and rhenium form $\sigma\text{-C}$ derivatives with perfluoroaromatic nitriles by nucleophilic attack of the ring at the para position to the cyano substituent (84, 85, 99, 100). Hydrogen abstraction was also involved in the formation of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{F}_3(\text{H})\text{CN}]$ from $\text{C}_6\text{F}_5\text{CN}$ (100).

1. Dialkylcyanamide Derivatives

The ambidentate cyanamides have the potential to bond through the amine lone pair, the nitrile lone pair, the nitrile π -system, or through a combination of these types. Dialkyl compounds were initially studied with nickel carbonyl and shown to produce complexes of the type $[(\text{R}_2\text{NCN})\text{Ni}(\text{CO})]_2$ [LXXI; $\text{R} = \text{Me}, \text{Et}, \text{Bu}$; $\text{R}_2 = (\text{CH}_2)_4$ or $(\text{CH}_2)_5$, $\text{C}_6\text{H}_4(\text{CH}_2)_3$, $\text{O}(\text{CH}_2\text{CH}_2)_2$] (74, 75). The π -system was originally considered to be delocalized and to donate four electrons to the metal (74), but subsequently bonding via the amine lone pair and $\text{C}-\text{N}$ π -system was suggested (75). An X-ray crystal structure of carbonyl(piperidine-*N*-carbonitrile)nickel



(LXXI)

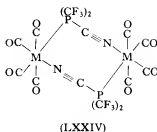
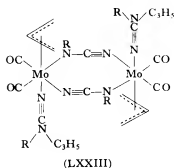


(LXXII)

(LXXII) showed neither description to be correct. The nickel atoms were attached to terminal carbonyl and bridging cyanamide groups with each nitrile group σ -bonding through the nitrogen lone pair to one nickel atom and bonding through the cyano- π -system to a second nickel atom. The nitrogen atom of the piperidine ring was not involved in bonding to nickel (320). The ν_{CO} for these complexes ($\sim 1790 \text{ cm}^{-1}$) was found to be extremely low for terminal groups in neutral complexes (75).

Photolytic or thermal reactions of dialkyl cyanamides with $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Cr}, \text{Mo}$) produced simple substitution products $[(\text{R}_2\text{NCN})_n\text{M}(\text{CO})_{6-n}]$ ($\text{M} = \text{Cr}, \text{Mo}$; $\text{R}_2 = (\text{CH}_2)_3, (\text{CH}_2)_4, (\text{CH}_2)_4\text{CHMe}, \text{O}(\text{CH}_2\text{CH}_2)_2$, and $(\text{C}_6\text{H}_{11})_2$, $n = 1, 2, 3$), in which only the nitrile lone pair σ -bonds to the metal. The increase in ν_{CN} was $25\text{--}53 \text{ cm}^{-1}$. The photolytic route at $20^\circ\text{--}30^\circ$ led to the mono- and disubstituted complexes ($n = 1, 2$), whereas the thermal route produced di- and trisubstitution ($n = 2, 3$). The ligands were found to be rather weakly bound; thus *cis*- $[(\text{R}_2\text{NCN})_2\text{Mo}(\text{CO})_4]$ reacted with PPh_3 with displacement of the cyanamide to give $[(\text{PPh}_3)_2\text{Mo}(\text{CO})_4]$ (76). The thermal reaction of allylcyanamides with $\text{Mo}(\text{CO})_6$ gave different products, to which structures such as (LXXIII; $\text{R} = \text{C}_3\text{H}_5$, Me) were assigned on the basis of IR and ^1H NMR. One allyl group was cleaved from the allylcyanamide to bond as a π -allyl group, while the cyanamido residue was believed to bridge between the two molybdenum atoms (169).

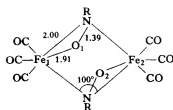
Related to dialkylcyanamides is the ligand $(\text{CF}_3)_2\text{PCN}$, for which similar bonding modes are possible. With $[\text{C}_7\text{H}_8\text{M}(\text{CO})_4]$ ($\text{M} = \text{Cr}, \text{Mo}$), dinuclear complexes $[\text{M}(\text{CO})_4\text{P}(\text{CN})(\text{CF}_3)_2]_2$ (LXXIV) were formed with bridging



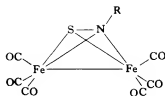
$\text{-P-C}\equiv\text{N-}$ units (379). The nitrile group apparently enters into strong π -bonding with the phosphorus and metal atoms and back-donation into antibonding orbitals causes ν_{CN} to be reduced by 40 cm^{-1} compared with the free ligand. Extensive π -interaction in the planar bridging system was indicated by the mass spectrum. The bridging unit remains intact up to the loss of eight carbonyl groups (379).

J. Nitroso and Nitroxide Derivatives

Organonitroso compounds and nitroxides are potential nitrogen and oxygen donors, or, as in the case of CF_3NO , potential sources of CF_3 and NO radicals (231, 402). Nitrosobenzene failed to react with iron carbonyls under forcing conditions, but heating or irradiation (UV or γ) of iron carbonyls in nitrobenzene produced nitroso-bridged complexes $[\text{PhNOFe}(\text{CO})_3]_2$. Initial formation of $[\text{PhNO}_2\text{Fe}(\text{CO})_4]$ was thought to occur followed by subsequent loss of carbon dioxide (246, 247). Mössbauer studies showed that for all complexes of the type $[\text{R}'\text{R}''\text{C}_6\text{H}_3\text{NOFe}(\text{CO})_3]_n$ the iron atoms have identical environments, and the complexes have similar structures (202, 220). The crystal structural determination confirmed a centrosymmetric dimeric structure (LXXV) for the 2-methyl-3-chloro derivative and showed the following novel features. The $\text{Fe}(\text{CO})_3$ units are bridged by the two RNO groups but only the nitrogen atoms are bonded to both iron atoms (planar Fe_2N_2 ring). Each oxygen atom is bonded to one iron atom but is distant from the second iron atom. The short metal-metal bonds normally associated with bridging nitrogen atoms cannot, according to this structure, be due exclusively to the presence of bridging nitrogen atoms (42). In the related complex $[\text{Fe}_2(\text{CO})_6(\text{RNS})]$, both bridging nitrogen and sulfur atoms were postulated (LXXVI) (393).



(LXXV)



(LXXVI)

Treatment of $[\text{PhNOFe}(\text{CO})_3]_2$ with PPh_3 caused cleavage of the bridges and formation of $[\text{PhNOFe}(\text{CO})_2\text{PPh}_3]$ (246). Electron-donating groups, particularly in ortho and para positions in the nitrobenzene ring, encouraged formation of monomeric complexes $[\text{ArylNOFe}(\text{CO})_3]$ in solution, and molecular weight measurement for *p*-MeO-, *p*- and *m*-CH₃, and *o*-(*o*'-NO₂C₆H₄) derivatives indicated both mono- and dinuclear species in benzene at 37°C (247).

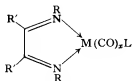
The parent group, HNO, was detected in the complex $[\text{OsCl}_2(\text{HNO})(\text{CO})(\text{PPh}_3)_2]$ formed through protonation of the coordinated nitrosyl group in $[\text{OsCl}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$ using hydrogen chloride. Carbon monoxide displaced HNO, but in solution the complex disproportionated with loss of HCl (243).

Brief mention has been made of the formation of $[(\text{CF}_3)_2\text{NOMn}(\text{CO})_3]$ from bis(trifluoromethyl) nitroxide and $[\text{Mn}(\text{CO})_5\text{H}]$, but only very limited detail was given (18).

K. Schiff Base Derivatives

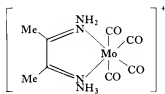
1. Azabutadiene Derivatives

The diazabutadiene complexes (LXXVII; M = Cr, Mo, W, R' = Me, Ph, R = OH, NH₂, Me₂N, alkyl, aryl, *x* = 3, L = CO; M = Fe, R' = Me, R = Ph, *tert*-Bu, *x* = 2, L = CO; M = Ni, L = CO, *x* = 1, R' = alkyl, R = NH₂, NR₂, OH, OR) were prepared from the metal carbonyls directly, or by displacing other groups such as dialkylcyanamides or the cycloheptatrienyl

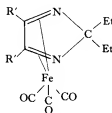


(LXXVII)

groups using the preformed ligand (77, 79, 392). Alternatively, the complexes were produced from the diketone, the carbonyl, and the appropriate amine, hydrazine, or hydroxylamine. With iodine and triphenylphosphine, carbon monoxide was displaced from the molybdenum complexes to give (LXXVII; $R = NH_2$, $R' = CH_3$, $L = I$, PPh_3), but benzylamine replaced the nitrogen substituents, forming (LXXVII; $L = CO$, $R = CH_2Ph$, $R = CH_3$) with displacement of hydrazine. Protonation with hydrogen halides gave the cation (LXXVIII) (77, 79). When chelate attachment of the diazobutadiene



(LXXVIII)



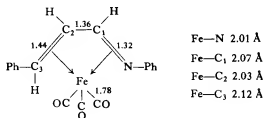
(LXXIX)

is prevented by incorporating the system into a five-membered ring, π -complexes of type (LXXIX; $R' = Me$, Et) are formed readily with $Fe_2(CO)_9$ in nonpolar solvents (168).

For the complexes $[(C_6H_{11}N:CHCH:NC_6H_{11})Mo(CO)_2LL']$ and $\{[NH_2N:C(Ph)C(O)Ph]Mo(CO)_2LL'\}$ ($L = L' = CO$, PPh_3 ; $L = CO$, $L' = PPh_3$), the CO stretching frequencies associated with the carbonyl groups trans to the azabutadiene ligands showed an unusually strong solvent dependence, whereas for those associated with the cis groups, the changes lie within experimental error. Thus solvent-dependent polarization occurs in the ground state in the direction of the twofold symmetry axis. The complexes were shown to have a delocalized group similar to many complexes of the four-center SCCS system (171a). A study of the transmission of electrical charge to and through a metal atom before and after electron

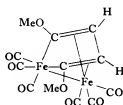
reduction of $[\text{W}(\text{CO})_4(\text{diacetylanil})]$ using IR spectroscopy showed a σ -directional mechanism to be operative in addition to π -transmission of charge density.

Azabutadienes ($\text{RCH}=\text{CHCH}=\text{NR}'$) with iron carbonyls gave complexes of the type $[(\text{RCH}:\text{CHCH}:\text{NR}')\text{Fe}(\text{CO})_3]$ which were assigned π -1,3-diene-type structures, analogous to butadieneiron tricarbonyl, on the basis of ^1H NMR studies (392). The crystal structure of $[(\text{PhCH}:\text{CHCH}:\text{NPh})\text{Fe}(\text{CO})_3]$ (LXXX) confirmed that the nitrogen lone pair does not play an important part in the bonding with the metal (160). With triphenyl-



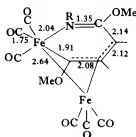
(LXXX)

phosphine, (LXXX; $\text{R} = \text{R}' = \text{Ph}$) gave $[(\text{PhCH}:\text{CHCH}:\text{NPh})\text{Fe}(\text{CO})_2\text{PPh}_3]$ in contrast to (LXXX; $\text{R} = \text{Me}$, $\text{R}' = n\text{-Bu}$), which gave free olefin and $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]$ (392). $[\text{RCH}=\text{CHCH}=\text{NR}']$ ($\text{R} = \text{Ph}$; $\text{R}' = \text{Ph}$, $p\text{-CH}_3\text{C}_6\text{H}_4$) reacted with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ under mild conditions to form $[(\text{RCH}:\text{CHCH}:\text{NR}')\text{Rh}(\text{CO})_2\text{Cl}]$, which converts to $[(\text{RCH}:\text{CHCH}:\text{NR}')_2\text{Rh}(\text{CO})\text{Cl}]$ on heating. The anils in these complexes bond through the nitrogen atom only (292). Displacement of the remaining carbonyl group was achieved with acetylenes in the presence of benzoyl azide to form $[(\text{RCH}:\text{CHCH}:\text{NR}')\text{RhCl}(\text{R}''\text{C}_2\text{R}'')]$ ($\text{R} = \text{Ph}$; $\text{R}' = \text{Ph}$, $p\text{-CH}_3\text{C}_6\text{H}_4$; $\text{R}'' = \text{CF}_3$, COOMe) (292). Reaction of N,N' -dichloro- p -toluenesulfonamide with the butadiene derivative (LXXXI) resulted in the insertion of the



(LXXXI)

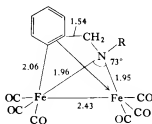
p -MeC₆H₄SO₂N unit into a metal-carbon bond of the ferrocyclopentadienyl ring (90). X-Ray crystallographic studies showed the complex to have structure (LXXXII; R = SO₂C₆H₄CH₃) (411).



(LXXXII)

2. Ortho-Metallated Aromatic Methyleneamine Derivatives

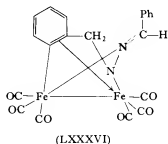
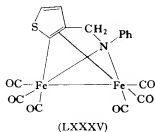
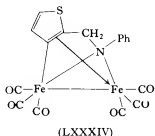
Ortho-metallation of compounds of the type Ph-X=NY (X = RC, N; Y = alkyl, aryl, OH, etc.) were discussed in Section F. Similar methyleneamine complexes, e.g., $\{[C_6H_4C(Ph)NPh]Mn(CO)_4\}$, have been produced (298), but the Schiff bases PhRC=NR' (R' = Ph, p -MeC₆H₄, N:CHPh; R = H, Ph, α -naphthyl, 2- and 3-thiophene) react with Fe₂(CO)₉ under mild conditions to form unusual complexes in which nitrogen acts as a bridging group between two metal atoms, and the σ -bonded ring system a two-electron π -donor to one metal (35, 36, 361, 405). The X-ray crystal structure confirmed the structure (LXXXIII; R = p -CH₃C₆H₄) (38),



(LXXXIII)

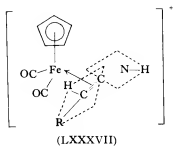
previously deduced by mass spectrometry, and from degradation to the amine and phthalimidine with LiAlH₄ and FeCl₃, respectively (35). Variations in R and R' did not appear to affect the reaction, except that reaction did not occur when the ortho positions were blocked (i.e.,

$\text{C}_6\text{F}_5\text{CH:NPh}$). Reaction proceeded even when the benzene ring was replaced by 2- and 3-thiophene to form (LXXXIV) and (LXXXV) (215). The related complex (LXXXVI) was prepared from $\text{Fe}_2(\text{CO})_9$ and the azine PhHC:NN:CHPh (392).

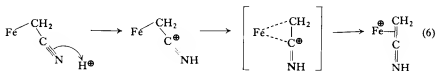


3. Ketenimine Derivatives

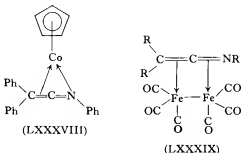
1-Cyanoalkyl complexes of the type $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{R})\text{C}\equiv\text{N}]$ ($\text{R} = \text{H}, \text{Me}$) were protonated with dry HCl to form cationic ketenimine derivatives $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{RCH}=\text{C}=\text{NH})]^+$ ($\text{R} = \text{H}, \text{Me}$) assigned structure (LXXXVII). The presence of two ν_{NH} , two $\delta(\text{NH})$ deformation



modes and two ^1H NMR signals arising from N—H protons suggested the presence of *exo* and *endo* isomers. The mechanism of protonation was considered analogous to that suggested for protonation of σ -allyl systems [Eq. (6)] and was supported by the inability of the 2-cyanoethyl derivatives to undergo similar protonation (26).

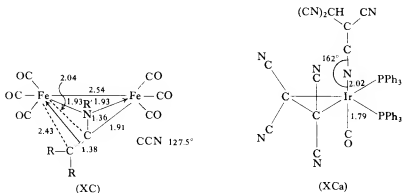


Reaction of the preformed ketenimine ligands $\text{Ph}_2\text{C}=\text{C}=\text{NR}$ ($\text{R} = \text{Ph}, \text{Me}$) with $[\text{Fe}_3(\text{CO})_{12}]$ and $[\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2]$ gave $[(\text{Ph}_2\text{C}=\text{C}=\text{NR})\text{Fe}_2(\text{CO})_6]$ ($\text{R} = \text{Ph}, \text{Me}$) and $[\pi\text{-C}_5\text{H}_5\text{Co}(\text{Ph}_2\text{C}=\text{C}=\text{NR})]$ ($\text{R} = \text{Ph}$), respectively. Structure (LXXXVIII), in which the C=C system and the nitrogen lone pair are involved in bonding, but not the C=N system, was tentatively suggested for the cobalt complex. For the iron complex structure (LXXXIX) was tentatively suggested on the basis of IR and ^1H NMR data but a recent X-ray crystal determination of $[(\text{Ph}_2\text{C}:\text{C}:\text{NMe})\text{Fe}_2(\text{CO})_6]$ (XC) showed



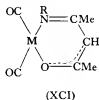
the organonitrogen ligand to bridge as an aza-allyl ligand (384b). Triphenylphosphine substitutes for one carbonyl group to form $[(\text{Ph}_2\text{C}:\text{C}:\text{NR})\text{Fe}_2(\text{CO})_5(\text{PPh}_3)]$ even with a large excess of ligand, suggesting coordinative saturation of the iron atoms (389). Insertion of tetracyanoethylene into metal alkyl or hydride bonds gave the ketenimino complexes $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{N}=\text{C}=\text{C}(\text{CN})\text{C}(\text{CN})_2\text{CH}_2\text{Ph}]$ (440a) and $\{\text{Ir}(\text{CO})[\text{C}_2(\text{CN})_4](\text{PPh}_3)_2\text{N}=\text{C}=\text{C}(\text{CN})\text{CH}(\text{CN})_2\}$, respectively. A crystal structural determination of the iridium complex (XCa) showed the Ir—NC₂ skeleton to be bent at nitrogen to the extent of $\sim 18^\circ$ from linearity (410a). Asymmetrical and

symmetrical stretching frequencies for the $\text{N}=\text{C}=\text{C}$ group were observed at 2151s and 1296s, respectively, for the iron complex (410a).



4. Methyleneamine and Related Derivatives

Treatment of $[\text{M}(\text{CO})_2\text{Cl}(\text{NH}_2\text{R})]$ ($\text{M} = \text{Rh}, \text{Ir}$; $\text{R} = \text{Ph}, p\text{-CH}_3\text{C}_6\text{H}_4, \alpha\text{-naphthyl}$) with acetylacetone gave the Schiff base complexes (XCI) (83), some of which exist in two different crystalline forms having different spectroscopic properties. Using the alternative preparative method of

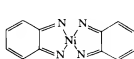


reacting $[\text{M}(\text{CO})_2\text{Cl}]_2$ ($\text{M} = \text{Rh}, \text{Ir}$) or $\text{Na}_2[\text{Ir}_2(\text{CO})_8\text{Cl}_{4.8}]$ with $[\text{MeCOCH}_2\text{C}(\text{=NR})\text{Me}]$, an intermediate unstable adduct $\{(\text{CO})_2\text{ClRh}[\text{MeCOCH}_2\text{C}(\text{Me})=\text{NPr}]\}$ was isolated (82, 83). Related Schiff base derivatives of ruthenium have been isolated also (114a, 185a).

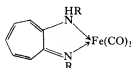
Nucleophilic attack at the carbon of a coordinated isonitrile molecule in the complex cations $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_{3-x}(\text{CNMe})_x]^+$ ($x = 1, 2$) using $\text{C}_6\text{F}_5\text{Li}$ produced *inter alia* the imino derivatives $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{L})\text{C}(\text{C}_6\text{F}_5)=\text{NMe}]$ ($\text{L} = \text{CO}, \text{CNMe}$). Chromatographic separation of the products gave the complex ($\text{L} = \text{CNMe}$) in two isomeric forms, shown by IR spectroscopy to arise from *cis* or *trans* orientation of the *N*-methyl group

with respect to the C=N bond (449). The related complexes $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{C}(\text{:NC}_6\text{H}_{11})\text{CH}_2\text{C}_6\text{H}_4\text{X}]$ ($\text{X} = p\text{-Cl, H, Me}$) arise from the reaction of the benzyl derivative with cyclohexyl isocyanide (467).

Nickel carbonyl reacts with *o*-quinoneimine with displacement of all the carbonyl groups to form $\text{Ni}(\text{N}_2\text{C}_6\text{H}_4)_2$ (XCII) (41), and $\text{Fe}(\text{CO})_5$ reacted with aminotropone imines to form (XCIII; $\text{R} = \text{Me, Et, Ph, } p\text{-MeC}_6\text{H}_4$).

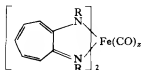


(XCII)

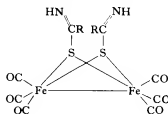


(XCIII)

Hydrogen and carbon monoxide were lost from the latter to form the Fe^{II} complexes (XCIV; $x = 0$). The appearance of an absorption assigned to ν_{MH} indicated the formation of an unstable Fe-H intermediate. Carbonylation of (XCIV; $x = 0$) gave the red cis complex (XCIV; $x = 2$) (344). Noncoordinate imine groups were postulated for the product (XCV; $\text{R} = p\text{-MeOC}_6\text{H}_4$) from the reaction of $\text{Fe}_2(\text{CO})_9$ and *p*-methoxythio-benzamide, which contrasts with the normal reaction of iron carbonyls with primary amides and thioamides, which proceed to nitriles (16).

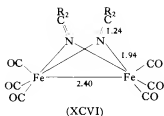


(XCIV)

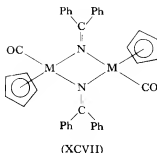


(XCV)

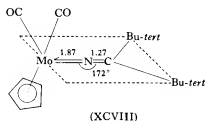
The compound $[\text{R}_2\text{C:NN:CR}_2]$ ($\text{R} = \text{CH}_3\text{C}_6\text{H}_4$) reacts with $\text{Fe}(\text{CO})_5$ to give the nitrogen-bridged methyleneamino complex $[(\text{CO})_3\text{FeN:CR}_2]_2$ (XCVI) (93). Treatment of $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{X}]$ ($\text{X} = \text{Cl, Br, I}$) with $\text{Me}_3\text{SiN:CRR}'$ or $\text{LiN:CRR}'$ gave complexes of three types: $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2\text{N:CRR}']$ ($\text{R} = \text{R}' = \text{Ph, } \textit{tert}\text{-Bu, } p\text{-CH}_3\text{C}_6\text{H}_4$; $\text{R} = \text{Ph, R}' = \textit{tert}\text{-Bu}$), $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})\text{N:RR}']_2$ (XCVII; $\text{R} = \text{R}' = \text{Ph}$), and $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2(\text{RR}'\text{CNCRR}')]$ ($\text{R} = \text{R}' = \text{Ph, } p\text{-CH}_3\text{C}_6\text{H}_4$) (187, 188, 293, 294, 299-301).



NFeN 77.0° av.
 FeNFe 77.1°
 Dihedral angle between FeNFe planes 70.4°



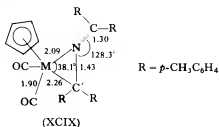
Considering the first type of complex, the Mo—N—C skeleton in [π -C₅H₅Mo(CO)₂N:CBu-*tert*₂] (XCVIII) was shown to be almost linear, and the molybdenum—nitrogen distance (1.87 Å) to be short (422) compared to the Mo—N single-bond distance (2.32 Å) in Mo(CO)₃(dien) (148a). The plane of the methyleneamino group adopts a staggered configuration similar to that found for carbene derivatives for which π -bonding to the metals is also postulated (349). Reversible IR and ¹H NMR spectral changes in the temperature range 28° to -45° were reported for this same methyleneamino complex and interpreted in terms of conformational changes about the multiple metal—nitrogen bond (299). The corresponding diphenyl derivatives (188), unlike the di-*p*-tolyl (293), di-*tert*-butyl (300), and *tert*-butylphenyl complexes (301), readily lose carbon monoxide to form the dinuclear complexes (XCVII; M = Mo, *cis*-CO groups; M = W, *trans*-CO groups). Their failure to react with neutral ligands under forcing conditions and apparent coordinative saturation suggested strong bonding in the



M₂N₂ ring and involvement of 10 electrons, required if the effective atomic number rule is satisfied. Treatment of diphenyl derivatives with iodine yielded [π -C₅H₅)₃M₂I₃O₄] (M = Mo, W) (188) but [π -C₅H₅M(CO)₂N:CRR'] (R = Ph, *tert*-Bu; R' = *tert*-Bu) gave the oxidation products

$[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})\text{I}_2(\text{N:CRR}')] (300, 301)$. The complex $[\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})(\text{PPh}_3)\text{N:C-}t\text{-BuPh}] (301)$ was the only simple substitution product obtained, and again illustrates the dependence of the properties of methyleneamino complexes on the substituent groups.

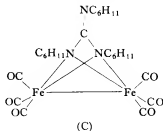
The stable complexes $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2(\text{R}_2\text{CNCR}_2)] (M = \text{Mo}, \text{W}; R = \text{Ph}, p\text{-CH}_3\text{C}_6\text{H}_4)$ contain an azaallyl or azaallene group rather than an aziridino group (187, 188, 294). The *p*-tolyl complex crystallized in two forms, but gave a common species in solution. Preliminary X-ray crystallographic data for one form showed the aza ligand to be bonded as an azaallene group (XCIX) (422), and the bonding to be best considered in terms of the



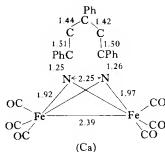
ion $[\text{R}_2\text{C}=\text{N}^+=\text{CR}_2]$ ($R = p\text{-CH}_3\text{C}_6\text{H}_4$) acting as a two-electron π -donor. The long $\text{C}'\text{—N}$ bond length, which approximates to a single-bond distance, indicates that the main interaction between the metal and the ligand is extensive $d\pi\text{—}\pi^*$ bonding arising from the charge on the ligand. ^1H NMR studies suggested σ, π -type bonding of an azaallyl group at -20°C in solution, and restricted rotation about the C—N single bond at higher temperatures. Mesomerism was thought to occur at $\sim 80^\circ\text{C}$ through interchange of the σ, π -bonding (293, 294). The manganese complex $[\text{Mn}(\text{CO})_4(\text{Ph}_2\text{CNCPh}_2)]$ and the related complex $\{\text{Mn}(\text{CO})_4[\text{Ph}_2\text{CN}(\text{H})\text{CPh}_2]\text{Br}\}$ were reported briefly (186). Treatment of the carbene complex $[(\text{CO})_5\text{CrC}(\text{OMe})\text{Me}]$ with hydroxylamines or a hydrazone $[\text{RR}'\text{C:NOH}]$ gave methyleneamine complexes of the type $[(\text{CO})_5\text{CrN}(\text{H}): \text{CRR}']$, which were shown by ^1H NMR spectroscopy to exist as cis and trans isomers relative to the C=N bond (197–199, 203, 209).

The carbodiimide $[\text{C}_6\text{H}_{11}\text{NCNC}_6\text{H}_{11}]$ reacted with $\text{Fe}(\text{CO})_5$ to form the red complex $[\text{Fe}_2(\text{CO})_6(\text{C}_6\text{H}_{11}\text{N})_2\text{C}] (\text{C}) (91)$, which can be considered to be the Schiff base derivative of a ureylene complex similar to (XIII). Rhodium(III) and iridium(III) carbonyl porphyrin complexes were prepared from $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and $\text{Ir}(\text{CO})_3\text{Cl}$, respectively (216, 217).

The iridium complex contained a tightly bound carbonyl group, unlike the rhodium complex, in accord with the stronger bonding of CO groups to 5d than to 4d transition metals (216). Related iron and ruthenium carbonyl porphyrins have also been described (14, 217, 461).



Ring cleavage occurred in the reaction of 3,5,7-triphenyl-4H-1,2-diazepine with $\text{Fe}_2(\text{CO})_9$, resulting in the rupture of the N—N bond. The Mössbauer spectrum of the product $\{\text{Fe}_2(\text{CO})_6[\text{N}:\text{C}(\text{Ph})\text{CHC}(\text{Ph})\text{CH}_2\text{C}(\text{Ph}):\text{N}]\}$ showed the two iron atoms to be in different environments, which was confirmed by a subsequent X-ray crystal determination. Unequal Fe—N distances were found (Ca), but the C—C distances in the chain bridging the two nitrogen atoms were found to be approximately the same rather than indicating the incorporation of a CH_2 unit (118).

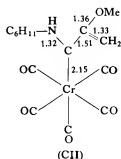
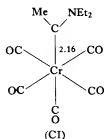


L. Phosphorimide Derivatives

$\text{Ph}_3\text{P}=\text{NH}$ acts as a neutral donor, displacing carbonyl and other ligands from molybdenum and tungsten complexes. Thus *cis*- $[(\text{Ph}_3\text{P}:\text{NH})_2\text{M}(\text{CO})_4]$ ($\text{M} = \text{Mo}, \text{W}$) and $[(\text{Ph}_3\text{P}:\text{NH})_2\text{Mo}(\text{CO})_3]_2$ were obtained from the hexacarbonyls, $[(\text{cycloheptatriene})\text{Mo}(\text{CO})_3]$, or $[(\text{C}_4\text{H}_8\text{NCN})_2\text{Mo}(\text{CO})_4]$ (76, 78).

M. Aminocarbene and Related Derivatives

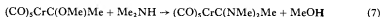
Although in aminocarbene complexes the metal is not directly bonded to nitrogen, nevertheless the nitrogen has considerable influence on the bonding between the carbon *p*-orbital and metal orbitals. The double-bond character of the latter bond in methoxy and phenoxy analogs is considerably reduced in the aminocarbenes by the increased donor character of nitrogen (204). Indeed in some aminocarbenes there is little M—C double bond character, as reflected by the observed bond length of 2.16 Å for [(CO)₅CrC(Me)NEt₂] (CI) (144), compared with 2.04 Å for [*cis*-L(CO)₄CrC(Me)(OMe)] [L = CO (349), PPh₃ (348, 350)], and the estimated Cr—C single-bond distance of 2.21 Å (144). However, metal-carbon distances do vary for aminocarbene derivatives depending on the nitrogen substituents, and a distance (2.09 Å) not significantly longer than for the alkoxycarbene derivatives was found for [(CO)₅CrC(Me)(NHMe)] (351). The crystal structure of {(CO)₅CrC(NHC₆H₁₁)[C(OMe):CH₂]} (CII) has a plane of symmetry through the CrCNC plane of the carbene, and a staggered



conformation (275) analogous to that of the other derivatives (37, 144). The complex *cis*-[PtCl₂[C(OEt)NHPh](PEt₃)], formed in the reaction of [PtCl₂(PhNC)(PEt₃)] with ethanol, has a Pt^{II}-carbene bond length of 1.98 Å, which for a Pt^{II} derivative indicates little participation of the metal in π -bonding to the carbene (32).

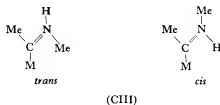
The synthesis of aminocarbene complexes was accomplished mainly either by treatment of the hexacarbonyl with lithium amides (204), followed by alkylation, or by treatment of carbene complexes with ammonia or

amines (141, 142, 209, 316, 356). Dimethylamine and diethylamine by the latter route (7) gave dialkylaminocarbene complexes, but *iso*-Pr₂NH and

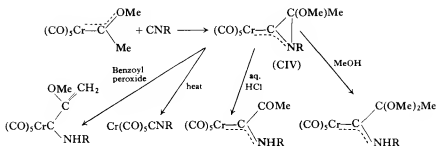


PhCH₂NHMe result in dealkylation and formation of Me(Me₂CHNH)C- and Me(PhCH₂NH)C- groups (141, 142). Hydroxylamine and hydrazines destroy the carbene group, forming methylenamine and nitrile complexes, respectively (Section II,K,4) (197-199, 203, 209). Second-order kinetics (first-order complex and first-order amine) were found for the aminolysis of [(CO)₅CrC(OMe)Ph] with RNH₂ (R = C₆H₁₁, *n*-Bu, CH₂Ph). Initial formation of a hydrogen-bonded adduct, which was detected by ¹H NMR measurements, was followed by nucleophilic substitution of a carbene oxygen atom by a second amine molecule (256).

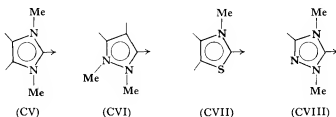
A mass spectral study of complexes of the type [(CO)₅CrC(NHR)Me] showed fragmentation to occur via successive loss of carbonyl groups to give [CrC(NHR)Me]⁺, the most abundant fragment (360). ¹H NMR studies of ¹⁵N-substituted [(CO)₅CrC(NH₂)Me] pointed to nonequivalent N—H protons and hindered rotation of the NH₂ group with a barrier to rotation greater than that of formamide (353). *Cis* and *trans* isomers were detected for methylamino derivatives [(CO)₄LMC(NHMe)Me] (M = Cr, L = CO; M = W, L = CO, PPh₃) (CIII) (354), isomerization of *cis*- to *trans* isomers being accomplished with bases. The reversible process is thought to proceed via an anion that is formed by abstraction of a proton from the nitrogen atom (355, 356).



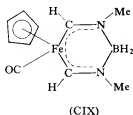
Insertion of isocyanide carbon atoms into the Cr—carbene bond of [(CO)₅CrC(OMe)Me] gave aziridinyldiene complexes (CIV), some reactions of which are summarized in Scheme 2 (28, 198). Cyclic carbene groups (CV)–(CVIII), in which the carbene carbon atom is part of an aromatic six-electron π -system, have been reported to form pentacarbonyl chromium and tetracarbonyl iron complexes (383, 384). Related to carbene



complexes is the product of the low-temperature reaction of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})_2]^+$ with sodium borohydride, which proceeds with $\text{B}-\text{H}$



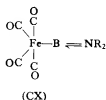
addition to the two $\text{C}-\text{N}$ groups. The delocalized structure (CIX) with six associated electrons was suggested (448). Ferrocenyl and azaferrocenyl-carbenes have recently been reported (143).



N. Aminoborylene Derivatives

Treatment of $\text{Fe}_2(\text{CO})_9$ with aminoboron dihalides $[\text{R}_2\text{NBX}_2]$; $\text{R} = \text{Me}$, Et ; $\text{X} = \text{Cl}$, Br) gave mono- and polynuclear derivatives $[\text{Fe}(\text{CO})_4\text{BNR}_2]$ (CX) and $[\text{Fe}(\text{CO})_4\text{BNR}_2]_n$. ^{11}B NMR and ν_{BN} studies of the volatile

monomer indicated the stabilization of the $[\text{BNR}_2]$ species to be due to both $\text{B}-\text{N}$ and $\text{Fe}-\text{B}$ π -bonding. The presence of a moderately strong π -electron-donating substituent ($\text{R}_2\text{N}, \text{F}$) on the boron was shown to be necessary since only the polynuclear complex with bridging borylene groups (CXI) was obtained with the other boron halides (291, 416). Diaminoboryl derivatives of a variety of metal carbonyls are also known (381, 382).

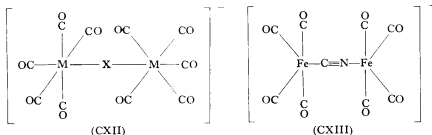


III

DERIVATIVES OF INORGANIC NITROGEN GROUPS

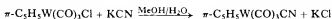
A. Cyano Derivatives

The cyanide ion is isoelectronic with carbon monoxide and like the latter readily forms complexes only with transition metals in oxidation states having electrons in d orbitals available for π -bonding (122, 423). Because of its negative charge, it is a poorer π -acceptor than carbon monoxide, although $d\pi-\pi^*$ bonding may still be important. The cyanide ion has unshared pairs of electrons on both the carbon and nitrogen atoms, but although bonding through the nitrogen lone pair has been established recently for terminal groups (104, 159), this bonding mode has not been found in cyano-carbonyl complexes. Terminal and bridging groups are well established (380), assignment of the mode of bonding often being based on ν_{CN} , which for terminal groups in neutral complexes occurs at $\sim 2100 \text{ cm}^{-1}$ and at lower frequencies in anionic complexes. Evidence for the presence of a bridging group has been based on an increase in ν_{CN} ($> 2130 \text{ cm}^{-1}$) (54, 179, 414). Linear CN bridges have been proposed for $[\text{M}_2(\text{CO})_{10}\text{CN}]^-$ ($\text{M} = \text{Cr}, \text{W}$) and $[\text{Fe}_2(\text{CO})_8\text{CN}]^-$ (414), the former with a staggered conformation (CXII; $\text{X} = \text{CN}$) (54, 329). The proposed structure of the iron complex (CXIII) is of particular interest since it differs from those of isoelectronic $\text{Fe}_2(\text{CO})_9$ and $[\text{Fe}_2(\text{CO})_8\text{H}]^-$, which have bridging carbonyl groups.

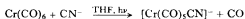


Cyano-carbonyl complexes have been synthesized by the following routes:

- (1) Metathetical replacement of halido by cyano groups (55, 166, 190, 270)



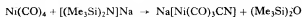
- (2) Thermal or photolytic displacement of CO and other ligands using CN^- (67, 369, 414)



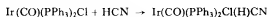
- (3) Reaction of a carbonylate salt with cyanogen or iodocyanogen (57, 127)



- (4) Substitution of a carbonyl oxygen atom using $\text{Na}[\text{N}(\text{SiMe}_3)_2]$ (101, 304, 462)



- (5) Oxidative addition of HCN (70, 424)



- (6) Treatment of a carbamoyl derivative with an amine (61)



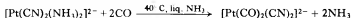
- (7) Deselenation of seleno-cyanato derivatives (280, 281)



- (8) Deprotonation of hydrogen cyanide adducts (304, 249)



- (9) Carbonylation of cyanide complexes (368)



- (10) Electrochemical methods (167)

Route (2) is that most used, but the final product often depends critically upon the choice of a thermal or photolytic process, the molar ratio of reactants, the reaction time and conditions. Behrens *et al.* used liquid

ammonia for the preparation of a large number of the complexes in Table II, but for many, alcohols are equally suitable. Substitution of nitrogen for a carbonyl oxygen atom was achieved using $\text{Na}[\text{N}(\text{SiMe}_3)_2]$ without cleavage of the metal-carbonyl bond. The mechanism of this remarkable reaction is not understood, but interestingly the reaction of $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ and $\text{Fe}(\text{CO})_5$, in contrast to that of the sodium salt, yielded $[(\text{CO})_4\text{FeCNSiMe}_3]$ (73).

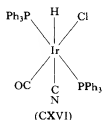
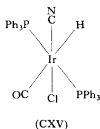
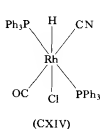
TABLE II
CYANO-CARBONYL COMPLEXES

Complex	References
$\{\pi\text{-C}_5\text{H}_5\text{V}(\text{CO})_3\text{CN}\}^-$	211-213
$[\pi\text{-C}_5\text{H}_5\text{V}(\text{CO})_2(\text{CN})_2]^{2-}$	211, 213
$[\text{M}(\text{CO})_5\text{CN}]^-$	M = Cr, Mo, W 56-58, 67, 167, 249, 304, 329, 414
$\text{cis-}[\text{M}(\text{CO})_4(\text{CN})_2]^{2-}$	M = Cr, Mo, W 53, 57, 58, 67, 414
$\text{Cr}(\text{CO})_5\text{CN}$	55, 329
$\text{cis-}[\text{M}(\text{CO})_3(\text{CN})_3]^{3-}$	M = Cr, Mo, W 53, 67, 257, 261
$\text{cis-}[\text{M}(\text{CO})_2(\text{CN})_4]^{4-}$	M = Cr, Mo, W 62
$[\text{M}_2(\text{CO})_{10}\text{X}]^-$	M = Cr, W 54, 57, 329, 414
$[\text{M}(\text{CO})_3\text{L}_2\text{CN}]^-$	M = Cr, Mo, W; $\text{L}_2 = \text{bipy}$, en, o-phen 58a, 59
$\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{CN}$	M = W 131, 166
$[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2(\text{CN})_2]^-$	M = Mo, W 131
$[\text{C}_6\text{H}_6\text{Cr}(\text{CO})_2\text{CN}]^-$	211
$[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})(\text{NO})\text{CN}]^-$	M = Cr, Mo, W 101
$\text{M}(\text{CO})_5\text{CN}$	M = Mn 127
$\text{cis-}[\text{M}(\text{CO})_4(\text{CN})_2]^-$	M = Mn, Re 19, 190, 270, 271
$\text{cis-}[\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{CN}]$	19
$[\text{Mn}(\text{CO})\text{L}_4\text{CN}]$	$\text{L}_4 = o\text{-(Ph}_2\text{PC}_6\text{H}_4)_3\text{P}$ 127
$[\text{M}(\text{CO})_3(\text{CN})_3]^{2-}$	M = Mn, Re 60, 64, 65
$\text{cis-}[\text{M}(\text{CO})_2(\text{CN})_4]^{3-}$	M = Mn, Re 60, 64, 65
$[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2\text{CN}]^-$	M = Mn 211
$\text{cis-Re}(\text{CO})_4(\text{NH}_2\text{Me})\text{CN}$	24
$\text{cis-Re}(\text{CO})_3(\text{NH}_3)_2\text{CN}$	60, 61
$\text{cis-}[\text{Re}(\text{CO})_3(\text{NH}_3)(\text{CN})_2]^-$	60
$[\text{Fe}(\text{CO})_4\text{CN}]^-$	414, 462
$[\text{Fe}_2(\text{CO})_8\text{CN}]^-$	414
$[\text{Fe}(\text{CO})(\text{CN})_5]^{3-}$	96, 147, 267, 268, 334, 357, 358
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CN}$	22, 109, 131, 280, 402, 403

TABLE II—continued
 CYANO-CARBONYL COMPLEXES

Complex		References
$[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CN})_2]^-$		131, 444, 450
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{L})\text{CN}$	$\text{L} = \text{PPh}_3$	281
$[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CN})_2]^{2-}$		131, 445
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNR})\text{CN}$		131
$[\text{Co}(\text{CO})(\text{CN})_5]^{3-}$		17
$[\text{Co}(\text{CO})\text{L}(\text{NO})(\text{CN})]^-$	$\text{L} = \text{CO}, \text{PMe}_2\text{Ph}$	63, 101a, 369
$[\text{Co}(\text{CO})(\text{NO})(\text{CN})_2]^{2-}$		63, 183
$\text{Co}(\text{CO})_2\text{L}_2\text{CN}$	$\text{L} = \text{PPh}_3, \text{PEt}_2\text{Ph}, \text{PPh}_2\text{Et}$	92
$[\text{Co}(\text{CO})\text{L}_2(\text{CN})_2]$	$\text{L} = \text{PPh}_3, \text{PEt}_2\text{Ph}, \text{PPh}_2\text{Et}$	92
$[\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})(\text{CN})]^-$		131
$[\text{Rh}(\text{CO})_2\text{CN}]_n$		326
$[\text{Rh}(\text{CO})(\text{CN})_3]^{2-}$		326, 332
$[\text{Rh}(\text{CO})_2(\text{CN})_2]^-$		326, 332
$\text{MCl}(\text{H})(\text{CO})\text{L}_2\text{CN}$	$\text{M} = \text{Rh}, \text{Ir}; \text{L} = \text{PPh}_3$	70, 424
$[\text{Ni}(\text{CO})_3\text{CN}]^-$		103, 462
$[\text{Ni}(\text{CO})_2(\text{CN})_2]^{2-}$		103, 367, 370
$[\text{Ni}(\text{CO})(\text{CN})_3]_2^{4-}$		103, 239, 240, 283, 333, 364-367, 370, 371
$[\text{Pt}(\text{CO})_2(\text{CN})_2]^{2-}$		368

Electrochemical generation of $[\text{M}(\text{CO})_5\text{CN}]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) was used in a study of their rates of reaction with ethyl bromide and methyl iodide. Their nucleophilicities were found to be by far the lowest for the series of complexes studied, and no alkyl derivatives could be formed (167). Hydrogen cyanide adds oxidatively to $[(\text{PPh}_3)_3\text{RhCl}]$ in the presence of carbon monoxide, and to $[\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}]$ to give $[\text{MCl}(\text{H})(\text{CN})(\text{CO})(\text{PPh}_3)_2]$ ($\text{M} = \text{Rh}, \text{Ir}$). (70, 424). Structures (CXIV) and (CXV) were proposed by Wilkinson *et al.* on the basis of ^1H NMR and deuteration studies, but Benzoni *et al.* report trans addition of HCN to form (CXVI) (70).



Irradiation of $[M(CO)_6]$ ($M = Cr, W$) in THF solution, followed by the addition of hydrogen cyanide, gave $[M(CO)_5NCH]$, which was deprotonated by piperidine to yield the cyano complexes $[PipH] [M(CO)_5CN]$. Deprotonation was accompanied by a change in bonding of the cyano group, and subsequent treatment with acid produced the isomeric isocyanic acid complexes $[M(CO)_5CNH]$ ($M = Cr, W$) (249), previously reported by King ($M = Cr, Mo, W$) (304). A similar protonation reaction was achieved with $[\pi-C_5H_5Mn(CO)_2CN]^-$ to form $[\pi-C_5H_5Mn(CO)_2(CNX)]$ ($X = H, ^2H$) (211).

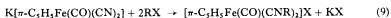
Carbonylation of cyanide complexes was achieved for $[Pt(CN)_2(NH_3)_2]^{2-}$ (368) and $[Fe(CN)_5X]^{n-}$ ($X = CN, n = 4$ (147, 357, 358); $X = NH_3, n = 3$) (268, 334), but some doubt exists about the claim that water can be displaced from $K_3[Fe^{II}(CN)_5 \cdot H_2O]$ (147, 267). The free acid $H_3[Fe(CO)(CN)_5] \cdot H_2O$ was isolated, but attempts to oxidize the complex to the unknown Fe^{III} complex failed (295).

Binuclear $[Rh(CO)_2Cl]_2$ reacts with cyanides in aqueous methanol to produce the non-carbonyl-containing anions $[HRh(CN)_5]^{3-}$ (319) and $[HRh(CN)_4(H_2O)]^{2-}$ (326, 332), but Wilkinson *et al.* (326) showed the intermediate in this reaction to be the polymeric cyano-carbonyl $[Rh(CO)_2CN]_n$, which has bridging cyano groups. Other cyano-carbonyls, $[Rh(CO)(CN)_3]^{2-}$ and $[Rh(CO)_2(CN)_2]^-$, were considered to be intermediates (to which methyl halides add oxidatively) in the formation of $[Rh(CN)_4(H_2O)Me]^{2-}$ from $[Rh(CO)_2Cl]_2$, NaCN, and methyl halides in dry methanol (332). The complex $[\pi-C_5H_5Fe(CO)_2]_2$ was reported to react with cyanide ions to form dianionic $[\pi-C_5H_5Fe(CO)(CN)_2]^{2-}$ (445), which if formulated correctly is unusual in that the ion exceeds the noble gas configuration by one electron. Oxidation with bromine gave the monoanionic complex (131).

Cryoscopic measurements on solutions of $K_4[Ni(CO)(CN)_3]_2$ (364), and the diamagnetism (370) indicated a dinuclear anion both in solution and the solid state, but the infrared spectrum was interpreted on the basis of both bridged carbonyl (365) and nonbridged structures (239). Recently the complex was shown to be an equimolar mixture of $K_2[Ni(CN)_4]$ and $K_2[Ni(CN)_2(CO)_2]$, which were precipitated separately from aqueous or liquid ammonia solutions as $[Ph_4P]^+$ salts (371).

Alkylation of cyano groups to form isonitrile complexes was achieved with alkyl bromides and iodides for the complexes $[\pi-C_5H_5Fe(CO)(CN)_2]^-$ [Eqs. (8) and (9)], $[\pi-C_5H_5M(CO)_3CN]$ ($M = Mo, W$), and $[\pi-C_5H_5Mo(CO)_2(CN)_2]^-$. Alkyl chlorides reacted slowly, but no reaction occurred

with aromatic halides (131). Although the cyano group of $[\text{M}(\text{CO})_5\text{CN}]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) was readily protonated, attempts at alkylation failed (304).



A comparison of ν_{CO} for $[\text{Mn}(\text{CO})_4(\text{CN})_2]^-$ with those of the corresponding halides showed the $\text{M}-\text{CN}$ bonding not to be drastically different from $\text{M}-\text{halogen}$ bonding, as may have been expected if CN^- was considered an extremely good π -bonding ligand, but the rate of reaction with PPh_3 to produce *cis*- $[\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{CN}]$ showed the cyano group to be much more strongly bound to manganese than any of the halides (19). The inability of the cyano group to strengthen the $\text{M}-\text{C}$ bond through π -bonding with the metal to the same extent as CO and NO is illustrated by the reaction of $[\text{Co}(\text{CO})(\text{NO})(\text{CN})_2]^{2-}$ with $(\text{Ph}_2\text{PCH}_2)_3\text{CH}$ in liquid ammonia. The cyano groups were replaced in preference to CO and NO (183).

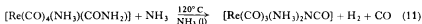
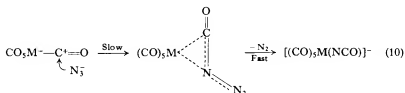
B. Cyanogen Derivatives

Cyanogen may undergo carbon-carbon bond cleavage and oxidative-addition reactions with transition metals to form dicyano complexes (25), or undergo reactions in which it acts as a bridging donor group. Photolytic reaction of cyanogen with $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) in THF gave the intensely colored, linearly bridged complexes $(\text{CO})_5\text{M}-\text{NCCN}-\text{M}(\text{CO})_5]$ (248).

C. Cyanato Derivatives

Although the reactions of cyanate ions with metal carbonyls and carbonyl halides produce isocyanato derivatives (e.g., $[\text{W}(\text{CO})_5\text{NCO}]^-$ (50), $[\text{Ru}(\text{PPh}_3)_2(\text{CO})(\text{NO})\text{NCO}]$ (322b), $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{NCO}]$ (81), $[\text{Mn}_2(\text{CO})_6(\text{NCO})_3]^-$, $[\text{Re}_2(\text{CO})_6(\text{NCO})_2(\text{N}_3)_2]^{2-}$ and $[\text{M}(\text{CO})_3(\text{PPh}_3)_2\text{NCO}]$ ($\text{M} = \text{Mn}, \text{Re}$) (338a)), the majority of known derivatives have been synthesized by a Curtius-type degradation route (50, 52, 109, 136, 138, 463). Nucleophilic attack at the carbon atom of a carbonyl group by azide ions produced molecular nitrogen and the complexes $[\text{M}(\text{CO})_5\text{NCO}]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) (50, 52, 463a), $[\text{Re}(\text{CO})_4(\text{MeNH}_2)\text{NCO}]$ (24), and $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})(\text{L})\text{NCO}]$ ($\text{M} = \text{Fe}, \text{Ru}$; $\text{L} = \text{CO}, \text{C}_2\text{H}_4$) (108, 109, 317, 321), the iron complex also being produced by displacement of ethylene by NCO^- in $[\pi\text{-C}_5\text{H}_5\text{Fe}$

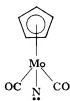
$(\text{CO})_2(\text{C}_2\text{H}_4)]^+$ (109). Interestingly, the azido complexes $[(\text{diolefin}) \text{RhN}_3]_2$, $[\text{M}(\text{PPh}_3)_2(\text{CO})\text{N}_3]$, ($\text{M} = \text{Rh}, \text{Ir}$) react with carbon monoxide to form the corresponding isocyanato derivatives (46, 48, 109a, 136). Mechanistic studies of the reaction of tungsten carbonyl with azide ions showed the second-order reaction (first order in both carbonyl and azide ion) to proceed by nucleophilic attack of the azide at the carbon atom of the CO group [Eq. (10)], followed by a synchronous rearrangement, release of nitrogen, and formation of the $\text{M}-\text{N}$ bond (52, 463). A small amount of $[\text{Re}(\text{CO})_3(\text{NH}_3)_2 \text{NCO}]$ was formed by treating $[\text{Re}(\text{CO})_4(\text{NH}_3)(\text{CONH}_2)]$ with ammonia at 120°C , according to Eq. (11) (61), but carbazoyl derivatives $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2(\text{CONHNH}_2)]$ ($\text{M} = \text{Fe}, \text{Ru}$) (321) and *cis*- $[\text{Re}(\text{CO})_4(\text{NH}_2\text{Me})(\text{CONHNH}_2)]$ (24) readily lose ammonia to give $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2\text{NCO}]$ and $[\text{Re}(\text{CO})_4(\text{NH}_2\text{Me})\text{NCO}]$, respectively.



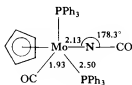
Irradiation of $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{NO})]$ in benzene solution in the presence of PPh_3 gave the isocyanato complex $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{NCO}]$ by a process consistent with the formation of the organometallic nitrene (CXVIIa) which captures carbon monoxide to produce the $-\text{NCO}$ group. Triphenylphosphine abstracted the nitrosyl oxygen atom, a process PPh_3 achieves with other coordinated groups. Irradiation of $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})(\text{PPh}_3)\text{LN}_3]$ ($\text{L} = \text{CO}, \text{PPh}_3$) in the presence of PPh_3 and under an atmosphere of carbon monoxide gave $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})(\text{PPh}_3)\text{LNCO}]$ ($\text{L} = \text{CO}, \text{PPh}_3$), which were prepared also by a metathetical route (317).

The X-ray crystal structure of $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})(\text{PPh}_3)_2\text{NCO}]$ (CXVIIb) showed the $\text{M}-\text{N}-\text{CO}$ skeleton to be closely linear and the PPh_3 groups to have a trans configuration. In solution, however, a mixture of *cis* and *trans* isomers was detected by IR spectroscopy (317). The crystal structure of $[\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{NCO}]$ (110, 112) again showed an approximately linear (178.6°) $\text{M}-\text{NCO}$ skeleton and a $\text{Cr}-\text{NCO}$ bond length (1.98 \AA)

shorter than that of $[\pi\text{-C}_5\text{H}_5\text{Mo(CO)(PPh}_3)_2\text{NCO}]$ (CXVIIb) to the appropriate extent, but close to that in the related NMe_2 -bridged complex



(CXVIIa)



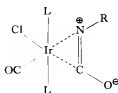
(CXVIIb)

$[\pi\text{-C}_5\text{H}_5\text{Cr(NO)NMe}_2]_2$ (III). Although shorter than the Cr—N distance of $[\text{Cr(CO)}_3(\text{dien})]$ (2.18 Å) (147a), it was thought unlikely that there is appreciable multiple bonding between the metal and nitrogen (110). All reported terminal cyanato groups in carbonyl complexes are N-bonded, although Burmeister *et al.* reported recently O-bonded groups in a series of d^0 complexes, $[(\pi\text{-C}_5\text{H}_5)_2\text{M(OCN)}_2]$ (M = Ti, Zr, Hf) (104, 105).

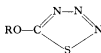
Treatment of iron carbonyls with organic azides (RN_3 ; R = Me, Et, Bu, Ph) gave ureylene, nitrene, and amino derivatives (Sections II, B, E, A) (164, 336). Ureylene derivatives were also formed from organic isocyanates (214, 336, 404), but with the chromium group hexacarbonyls, PhNCO gave low yields of isocyanate complexes which were not identified (336). Acyl azides (RCON_3) reacted with $[(\text{PPh}_3)_2\text{Ir(CO)Cl}]$ in chloroform containing traces of alcohol to form $[(\text{PPh}_3)_2\text{Ir(N}_2\text{)Cl}]$ (R = α -furyl, Ph, $p\text{-NO}_2\text{C}_6\text{H}_4$, $p\text{-CH}_3\text{C}_6\text{H}_4$, $p\text{-CH}_3\text{OC}_6\text{H}_4$) (134, 137, 138). The reaction was thought to proceed via the 1,3-dipolar intermediate (XXVI). In alcohol-free solvents the acyl isocyanate formed as an intermediate attacks the nitrogen complex to form the acyl isocyanate complex (CXVII), which on carbonylation gave (CXVIII; R = α -furoyl) (138). Characteristic



(CXVII)



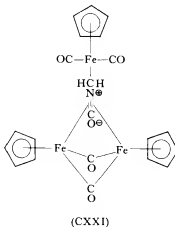
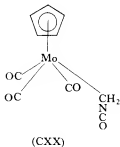
(CXVIII)



(CXIX)

absorptions in the 1600–1720 cm^{-1} and 1350–1410 cm^{-1} IR region were associated with antisymmetric and symmetric stretching frequencies of the π -bonded isocyanate group (137, 138). In an attempt to trap nitrogen from the decomposition of 5-ethoxy-1,2,3,4-thiatriazoles (CXIX), using $[\text{M}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$ ($\text{M} = \text{Ir}, \text{Rh}$), $[\text{M}(\text{PPh}_3)_2(\text{CO})(\text{NCO})]$ were isolated, possibly through reaction with EtOCN , also formed as a decomposition product (282). Cyanoolefins and hydrogen chloride added readily to *trans*- $[(\text{Ph}_3\text{E})_2\text{Ir}(\text{CO})\text{NCO}]$ ($\text{E} = \text{P}, \text{As}$) to give $[(\text{Ph}_3\text{E})_2\text{Ir}(\text{CO})\text{NCO}(\text{cyanoolefin})]$ and *cis*- and *trans*- $[(\text{PPh}_3)_2\text{Ir}(\text{CO})\text{NCO}(\text{H})\text{Cl}]$, respectively (30, 71).

Chloromethyl isocyanate reacts with $[\text{NaMo}(\text{CO})_3(\pi\text{-C}_5\text{H}_5)]$ to form the alkyl complex $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CH}_2\text{NCO}]$ (CXX), but a similar complex of iron could not be formed. Instead, $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]\text{Na}$ gave a mixture of products containing $[(\pi\text{-C}_5\text{H}_5)_3\text{Fe}_3(\text{CO})_4\text{CH}_2\text{NCO}]$. On the basis of IR and ^1H NMR studies, the dipolar resonance structure (CXXI) was suggested, in which the π -bonded isocyanate group bridges between two metals. This type of bonding is known for the isoelectronic $\text{C}\equiv\text{C}$ - group (309).



D. Fulminato Derivatives

Irradiation of $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) with fulminate ions in THF solution produced the first low-valent fulminato derivatives, *cis*- $[\text{M}(\text{CO})_4(\text{CNO})_2]^{2-}$ (51).

E. Thiocyanato Derivatives

The ambidentate thiocyanato group, in bonding through nitrogen or sulfur, provides a metal with the choice of a hard (type a) or a soft (type b) base with which to coordinate (380). The type of linkage has been shown to depend on steric properties (194, 417) and the various factors affecting the "hardness" of the metal in the complex (194, 446), for example, the oxidation state (193, 194, 466), extent of replacement of carbon monoxide by ligands of a lower π -acceptor capacity (194), and the nature of these ligands (194, 417). A delicate balance of both electronic and steric factors appears to govern the mode of attachment (194), and changes in the bonding have been observed for small changes in coordination at the metal (194). Thiocyanato groups in complexes containing strongly π -bonding ligands and those with metals in high oxidation states bond in general through sulfur, whereas in complexes in which the metal is able to strongly π -bond to the ligands, i.e., when carbon monoxide is replaced by better σ -donors but poor π -acceptors, N-bonding is observed (194). π -Bonding and "soft acid-base" arguments may be used to rationalize the bonding through either the nitrogen or sulfur (194, 279). Steric considerations are also important, since although the M—NCS skeleton is linear, that of the S-bonded form is bent ($\sim 120^\circ$ at sulfur) (226). Thiocyanato-carbonyl complexes are summarized in Table III.

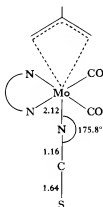
Various criteria have been used to deduce the type of bonding, the position of ν_{CS} and the integrated intensity of the ν_{CN} absorption being more reliable than the position of ν_{CN} . Absorptions (ν_{CS}) in the region 720–690 cm^{-1} and ν_{CN} intensities of $0.8\text{--}2.3 \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-2}$ are characteristic of S-thiocyanato groups, whereas absorptions in the region 780–860 cm^{-1} and ν_{CN} intensities $9\text{--}12 \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-2}$ are characteristic of N-bonded groups (426). N- and S-thiocyanato groups normally have ν_{CN} in the range 2040–2080 and 2080–2120 cm^{-1} , respectively, but exceptions do occur (380, 426). Bridging groups absorb between 2153 and 2162 cm^{-1} (279).

Both N- and S-bonded isomers were isolated for $[\text{Mn}(\text{CO})_5\text{CNS}]$ (193, 465), $[\text{Mn}(\text{CO})_4(\text{AsPh}_3)\text{CNS}]$ (194), $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3(\text{CNS})]$ (426), and $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CNS})]$ (426, 450). Although all the complexes were normally obtained in the S-form, isomerization of the first three complexes was effected in acetonitrile solution. In contrast, $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{SCN})]$ isomerized in the solid state but not in solution, and it was thought that an activated complex involving bridging thiocyanato groups was involved in the process, requiring an ordered and close arrangement of molecules (426).

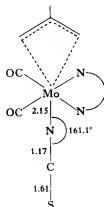
TABLE III
 THIOCYANATO-CARBONYL COMPLEXES

Complex		References
$[M(CO)_5NCS]$	M = Cr, Mo, W	55
$[Cr(CO)_5NCS]^-$	M = Mo, W also	66, 414, 450, 466
$[Cr_2(CO)_{10}CNS]$		54, 66
$[Cr_2(CO)_{10}CNS]^-$	M = W also	54
$[Mo(CO)_2(NCS)_2]_x$	M = W also	139
<i>cis</i> - $[Mo(CO)_2L_2(NCS)_2]$	L = PPh_3 , $(Ph_3P)_2CH_2$	139
$[\pi-C_5H_5Mo(CO)_3NCS]$	-SCN also, M = W also	426
$[\pi-AllylM(CO)_3L_2NCS]$	$\pi-Allyl = C_3H_5$, $CH_3C_3H_4$; $L_2 = bipy$, <i>o</i> -phen; M = Mo, W	226, 227, 274
$[Mn(CO)_5SCN]$	-NCS also	193, 465
<i>cis</i> - $[Mn(CO)_4LSCN]$	L = PPh_3 , $AsPh_3$, $SbPh_3$	194, 450
<i>cis</i> - $[Mn(CO)_3L_2NCS]$	L = Py, <i>p</i> -fan, γ -pic, <i>p</i> -tol; $L_2 = bipy$, diphos	193, 194, 466
<i>cis</i> - $[Mn(CO)_3L_2SCN]$	L = $AsPh_3$, $SbPh_3$	194, 465
<i>trans</i> - $[Mn(CO)_3L_2NCS]$	L = PPh_3 , $AsPh_3$, $SbPh_3$	194, 465
<i>cis</i> - $[Mn(CO)_4(NCS)_2]^-$		190, 450
$[Mn_2(CO)_8(CNS)_4]^{2-}$		190
<i>fac</i> - $[Re(CO)_3(NCS)_3]^{2-}$		450
$[Re(CO)_4(NCS)_4]^-$		148
$[Fe(CO)_4NCS]^-$		414
$[Fe(CO)_2L_2(NCS)_2]$	L = PEt_3	86
$[\pi-C_5H_5Fe(CO)_2NCS]$	-SCN also	22, 426, 450
$\pi-C_5H_5Ru(CO)_2NCS$		321
$[Ru(PPh_3)_2(CO)(NO)NCS]$		322b
$Os_3(CO)_{10}(SCN)(AuPPh_3)$		89
$[Rh(CO)_2SCN]_2$		279, 327
$[Rh(CO)_2(SCN)_2]^-$		279
$Rh(CO)L_2CNS$	L = PPh_3 , $AsPh_3$, $SbPh_3$, phosphites, Et_3PPh	124, 241, 279
$[Rh(CO)L(CNS)_2]$	L = Ar_3As , $(PhO)_3P$	279
$Rh(PPh_3)_2(CO)XY_2$	X, Y = Cl, Br, I, SCN	425
$Rh(CO)(Ph_3P)(SCN)SO_2$		241
$Ir(CO)L_2(SCN)HX$	L = PPh_3 ; X = Cl, <i>cis</i> and <i>trans</i>	71, 458
$Ir(CO)L_2(NCS)(olefin)$	L = PPh_3 , $AsPh_3$; olefin = $C_2(CN)_4$, $CH_2:CHCN$, $C_2H_2(CN)_2$	30

The X-ray crystal structures of $[\pi\text{-C}_3\text{H}_5\text{Mo}(\text{CO})_2(\text{bipy})\text{NCS}]$ (CXXII) (226) and $[\pi\text{-C}_4\text{H}_7\text{Mo}(\text{CO})_2(o\text{-phen})\text{NCS}]$ (CXXIII) (227) showed the *N*-thiocyanato groups to deviate from linearity. $\text{M}-\text{N}-\text{CS}$ bond angles of 176° and 161.1° , respectively, were found, the bend surprisingly being towards the chelate nitrogen ligand in *cis* positions (226, 227).

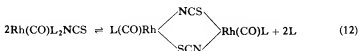


(CXXII)

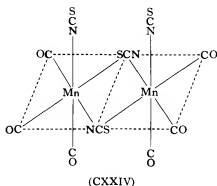


(CXXIII)

Preference for N-bonding in $[\text{Mn}(\text{CO})_3\text{L}_2(\text{NCS})]$ complexes was thought to arise from the increased extent of $\text{M}-\text{CO}$ π -bonding, resulting from replacement of carbon monoxide by good σ -donor ligands (194). The negative charge of $[\text{M}(\text{CO})_3\text{NCS}]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) similarly resulted in *N*-thiocyanato groups (66, 414, 450), but interestingly the corresponding neutral paramagnetic ($\mu \sim 1.7$ BM) chromium complex was also N-bonded (55). Both neutral and anionic dinuclear chromium complexes have been prepared with bridging thiocyanato groups. Oxidation of $[\text{Cr}(\text{CO})_5\text{NCS}]^-$ with ferric chloride gave paramagnetic $[\text{Cr}_2(\text{CO})_{10}\text{CNS}]$ ($\mu = 1.75$ BM) (54, 66) which was reduced by sodium amalgam to $[\text{Cr}_2(\text{CO})_{10}\text{CNS}]^-$ ($\mu = 3.02$ BM) (54). Bridged complexes were detected also in solutions of $[\text{Rh}(\text{CO})\text{L}_2\text{NCS}]$ [$\text{L} = \text{arylarsines}, (\text{PhO})_3\text{P}$] due to equilibrium [Eq. (12)] (279).



The dinuclear anion $[\text{Mn}_2(\text{CO})_6(\text{CNS})_4]^{2-}$ has been assigned structure (CXXIV) with two bridging thiocyanato groups and two cis-N-bonded terminal groups (190).



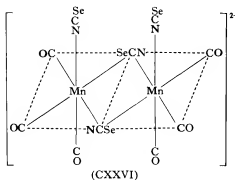
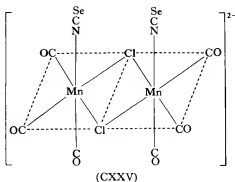
F. Selenocyanato Derivatives

Studies of the CNSe group as a ligand, particularly in noncarbonyl complexes, have shown the mode of the bonding to be much less sensitive to the presence of other ligands than with the corresponding thiocyanate (104, 280, 380). Isomerization between N- and Se-bonded selenocyanato-carbonyl complexes has been established by IR studies (281), and bridging SeCN groups have been suggested (190). Assignment of the bonding mode has been based primarily on the C—N and C—Se stretching frequencies, and the intensity of the absorptions. Se-bonded groups normally have a low intensity ($\sim 10^4$ l mole $^{-1}$ cm $^{-2}$) absorption for $\nu_{\text{CN}} > 2100$ cm $^{-1}$, and ν_{CSe} at 600–700 cm $^{-1}$, whereas N-bonded groups have $\nu_{\text{CN}} \leq 2100$ cm $^{-1}$ (intensity $\sim 5\text{--}10 \times 10^4$ l mole $^{-1}$ cm $^{-2}$) and ν_{CSe} at 500–530 cm $^{-1}$ (107, 190). The position of ν_{CN} is not a reliable criterion for differentiating between these two modes of attachment (281), and ν_{CSe} is to be preferred (190). Corresponding frequencies associated with bridging CNSe groups are not so well established, but compared with the free ion both ν_{CSe} and ν_{CN} are higher (104, 452).

Two general methods have been used to synthesize selenocyanate derivatives, namely the metathetical replacement of halogens with KSeCN, and the treatment of a carbonyl halide or alkyl with $\text{Se}(\text{SeCN})_2$ (190, 280, 281). Se-bonded structures were assigned to $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SeCN}]$ and to $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{SeCN}]$ (M = Mo, W) (280), but interestingly an

N-bonded structure was assigned to $[\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{NCSe}]$ (280). Both N- and Se-bonded forms of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{PPh}_3)\text{CNSe}]$ were isolated and found to be stable with respect to interconversion at ambient temperatures, but at higher temperatures, deselenation occurs to yield the corresponding cyano complex in preference to isomerization (281). Deselenation occurs for N-bonded groups in particular (280, 281), and the increased rate of deselenation of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SeCN}]$ in the presence of PPh_3 (281) possibly indicates conversion to the N-bonded form as an intermediate stage. Reactions of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SeCN}]$ with phosphines at ambient temperature caused the displacement of the selenocyanate ion to form $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{PR}_3)]\text{SeCN}$ ($\text{R} = \text{Ph}, \text{C}_6\text{H}_{11}$) but in refluxing benzene displacement of CO occurred to form $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{PR}_3)\text{SeCN}]$ ($\text{R} = \text{Ph}, \text{OPh}$) (281).

$\text{Mn}(\text{CO})_5\text{Cl}$ and KSeCN gave the anionic complexes $[\text{Mn}_2(\text{CO})_6\text{Cl}_2(\text{NCSe})_2]^{2-}$ and $[\text{Mn}_2(\text{CO})_6(\text{CNSe})_4]^{2-}$, assigned structures (CXXV) and (CXXVI) with bridging chloro- and selenocyanato groups, respectively,



and N-bonded terminal selenocyanato groups. No isomerization was detected (190).

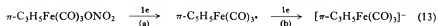
trans-[Rh(PPh₃)₂(CO)NCSe] provided the first example of cooperative electronic ligand control of the bonding mode of the CNSe group in square-planar complexes, which had been established previously for thiocyanato complexes. An N-bonded selenocyanato group was established by IR spectroscopy, and compared with the Se-bonding found in the sterically similar *trans*-[Pd(PPh₃)₂(SeCN)₂], the antisymbiotic switch to N-bonding was ascribed to the presence of CO. The corresponding iridium complex decomposed before it could be isolated, but the five-coordinate complex [Ir(PPh₃)₂(acetone)(CO)(NCSe)] was characterized (106).

G. Nitrate Complexes

Compatibility of potential oxidizing (–ONO₂) and reducing (CO) groups coordinated to the same metal was demonstrated by the isolation of [M(CO)₅ONO₂] (M = Mn, Re) from the reactions of M₂(CO)₁₀ with N₂O₄ (3–5, 9, 10, 12). The manganese complex was obtained also from treatment of [σ-CH₂:CHCH₂Mn(CO)₅] with nitric acid (235). Unidentate nitrate groups were established by IR and a single-crystal X-ray study of [Re(CO)₅NO₃] (273), but in the mass spectrum of the latter complex, the formation of [M(CO)_xO₂]⁺ ions possibly indicates rearrangement processes in the spectrometer to produce bidentate nitrate groups which subsequently lose NO. The primary fragmentation process is loss of NO₂ followed by subsequent loss of CO groups (5). Substitution reactions of [Mn(CO)₅ONO₂] with a variety of neutral nitrogen, phosphorus, and arsine ligands gave complexes of the type [M(CO)₄L(NO₃)] (L = PPh₃, AsPh₃), [Mn(CO)₃L₂(NO₃)₃] (*cis*, L = Py, PPh₃, L₂ = bipy; *trans*, L = PPh₃, *cis*-[Mn(CO)₃L₂L']NO₃ (L₂ = bipy, L' = Py, PPh₃), and [Mn(CO)₂L₂L']NO₃ (L₂ = bipy, L' = PPh₃) (6, 7). Certain PPh₃ and AsPh₃ complexes, viz., [Mn(CO)₄LNO₃] (L = PPh₃, AsPh₃) and *trans*-[Mn(CO)₃(PPh₃)₂(NO₃)] had unusual nitrate absorptions in the IR spectrum, and it was tentatively suggested that the nitrate group in these complexes may have local C_{3v} symmetry. Interestingly, the bonding of the nitrate group of [Mn(CO)₄(AsPh₃)NO₃] reverts to the unidentate type on aging in solution; at the same time changes in ν_{CO} indicate possible formation of a five-coordinate species through loss of the arsine ligand (7).

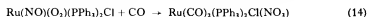
Oxidative fission of the metal-metal bond in [π-C₅H₅Fe(CO)₂]₂ with

anhydrous ferric perchlorate in acetone yielded solutions of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{Me}_2\text{CO})]^+$, which on treatment with nitrate ion gave $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{NO}_3]$ (287). Treatment of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_3\text{I}]$ with silver nitrate in $\text{MeNO}_2/\text{MeOH}$ produced $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_3\text{ONO}_2]$ (374, 375), which, on the basis of ^1H NMR studies, was considered to be either dissociated completely or to exist as weakly bonded ion pairs (377). However, a polarographic study showed the reduction process [Eq. (13)] to occur at more negative potentials than for the corresponding nonionic halo derivatives, which is consistent only with $\text{Fe}-\text{ONO}_2$ bonding (244). Decomposition of the complex in aqueous methanol at 70°C has been studied in detail



and shown to produce $\text{Fe}(\text{CO})_5$ and a mixture of aldehydes and ketones (374, 376).

Nitric acid replaced the hydrido group in $[\text{RuH}(\text{CO})(\text{PR}_3)_3\text{Cl}]$ to form the unidentate nitrate complex, *mer*- $[\text{Ru}(\text{CO})(\text{PMe}_2\text{Ph})_3(\text{ONO}_2)\text{Cl}]$ (330), whereas $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\text{NO}_3)\text{Cl}]$ was produced in a most intriguing reaction [Eq. (14)] in which coordinated nitrosyl and oxygen molecules react to produce the nitrate group (322). Coordinated oxygen in the Ir^{I}



complex $[(\text{Ph}_3\text{E})_2\text{Ir}(\text{CO})(\text{O}_2)\text{Cl}]$ ($\text{E} = \text{P}, \text{As}$) reacted with nitrogen dioxide to form the dinitrato- Ir^{III} complex $[(\text{Ph}_3\text{E})_2\text{Ir}(\text{CO})\text{Cl}(\text{NO}_3)_2]$ (328), formed also in the reaction of *trans*- $[\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}]$ with concentrated nitric acid (424).

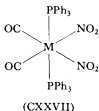
Studies of ν_{CO} for a series of square-planar complexes, *trans*- $[\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{X}]$ ($\text{X} = \text{halides}, \text{NO}_3, \text{SCN}$) and pyramidal complexes $[\text{Rh}(\text{PPh}_3)(\text{CO})\text{X}(\text{SO}_2)]$ showed the order of increasing frequencies to remain the same for the two series except for the nitrate complexes. This evidence was cited for π -interaction between the bonding π -orbital of the nitrate group and the p_z orbital of rhodium in the four-coordinate complex. However, this is not possible in the five-coordinate complex since the p_z orbital participates in σ -bonding with the unshared electron pair of sulfur (241).

H. Nitro and Nitrito Derivatives

$[\text{Mn}(\text{CO})_5\text{NO}_2]$ and $[\text{Mn}(\text{CO})_5\text{ONO}]$ were obtained as secondary products in the reaction of $\text{Mn}_2(\text{CO})_{10}$ and N_2O_4 in petroleum ether (10)

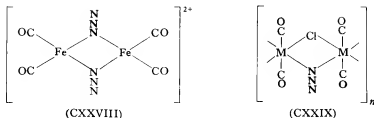
or in the vapor state. The small amount of isolated material, identified by IR spectroscopy and limited analytical data, reacted with 2,2'-bipyridyl and triphenylphosphine to give $[\text{Mn}(\text{CO})_3\text{L}_2\text{NO}_2]$ ($\text{L}_2 = \text{bipy}, 2\text{PPh}_3$) (8). The compounds $[\text{Re}(\text{CO})_5\text{ONO}]$ and $[\text{Re}(\text{CO})_5\text{NO}_2]$ were detected also by IR spectroscopy in the product formed from the arrested reaction of $\text{Re}_2(\text{CO})_{10}$ with N_2O_4 (5). The polymeric complex $[\text{Ru}(\text{CO})_2(\text{NO}_2)_2]_n$ was formed in the reaction of moist NO with $\text{Ru}_3(\text{CO})_{12}$ in refluxing dichloromethane solution. The IR absorptions assigned to the NO_2 group closely resemble those found for groups coordinated through both oxygen atoms, and a structure similar to that of the bridging halide complexes $[\text{Ru}(\text{CO})_2\text{X}_2]_n$ was suggested (116).

Attempts to synthesize nitro derivatives by metathetical and related processes have been notably unsuccessful, the nitrite ion oxidizing carbonyl groups to produce carbon dioxide and the corresponding nitrosyl derivative (265). Indeed this is a long-established method for synthesizing carbonyl nitrosyl complexes. Although the mechanism has not been definitely established, nitro complexes were considered to be intermediates (265). Reaction of $[\text{M}(\text{CO})_2(\text{PPh}_3)_2\text{Cl}_2]$ ($\text{M} = \text{Ru}, \text{Os}$) with sodium nitrite gave initially the dinitrito complexes $[\text{M}(\text{CO})_2(\text{PPh}_3)_2(\text{ONO})_2]$ which were shown to isomerize to the dinitro complex (CXXVII). Oxygen transfer to carbon monoxide and PPh_3 resulted in the formation of the dinitrosyl complexes $[\text{M}(\text{NO})_2(\text{PPh}_3)_2]$ ($\text{M} = \text{Ru}, \text{Os}$) (242).

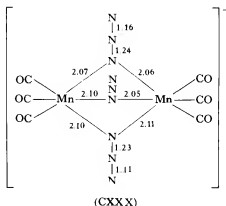


1. Azido Derivatives

Chlorine and bromine azides (N_3X) react with $\text{Fe}(\text{CO})_5$ in an inert solvent at -20°C to form $[\text{Fe}(\text{CO})_2\text{N}_3]_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$), which exhibit the highest paramagnetism (5.29 BM) known for metal carbonyl derivatives. A planar Fe_2N_2 ring system (CXXVIII) was postulated on the basis of IR studies. With $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Mo}, \text{W}$), chlorine azide in solution at ambient temperatures gave $[\text{M}(\text{CO})_2\text{N}_3\text{Cl}]_n$, assigned polymeric structures (CXXIX)



with chlorine and nitrogen bridges, on the basis of magnetic and IR evidence (324). Metathetical reactions were used to synthesize $[\text{Ru}(\text{PPh}_3)_2(\text{CO})(\text{NO})\text{N}_3]$ (322b), $[\text{M}(\text{CO})_3(\text{PPh}_3)_2\text{N}_3]$ ($\text{M} = \text{Mn}, \text{Re}$) (46, 338a, 463a), $[(\text{CO})_2\text{RhN}_3]_2$ (109a), $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})\text{I.L}'\text{N}_3]$ ($\text{L} = \text{PPh}_3$, $\text{L}' = \text{CO}$, PPh_3), and $[(\text{Ph}_3\text{P})_2\text{M}(\text{CO})\text{N}_3]$ ($\text{M} = \text{Rh}, \text{Ir}$). Oxidative addition of HCl to the latter complex ($\text{M} = \text{Ir}$) gave $[(\text{PPh}_3)_2\text{Ir}(\text{CO})\text{N}_3(\text{H})\text{Cl}]$ (71), whereas azido bridged complexes $[(\text{PPh}_3)_2(\text{CO})\text{M}(\text{N}_3)\text{M}(\text{CO})(\text{PPh}_3)_2]^+$ ($\text{M} = \text{Rh}, \text{Ir}$) were formed on treatment with oxonium or nitrosyl salts (338a). Treatment of $[(\text{C}_7\text{H}_8)\text{M}(\text{CO})_3]$ ($\text{M} = \text{Mo}, \text{W}$) with N_3^- in the presence of neutral chelate bases ($\text{L}_2 = \text{en}, \text{bipy}$) gave $[\text{M}(\text{CO})_3\text{L}_2\text{N}_3]^-$ (59) and irradiation of $\text{W}(\text{CO})_6$ in THF with subsequent addition of N_3^- gave $[\text{W}(\text{CO})_5\text{N}_3]^-$ (463a). Both azido and mixed azido-cyanato complexes were formed in the reactions of manganese and rhenium carbonyl halides with N_3^- , the products $[\text{Mn}_2(\text{CO})_6(\text{N}_3)_3]^-$ (CXXX), $[\text{Mn}_2(\text{CO})_6(\text{N}_3)_x(\text{NCO})_{3-x}]^-$,



$[\text{Re}_2(\text{CO})_6(\text{N}_3)_2(\text{NCO})_2]^{2-}$, $[\text{Mn}_2(\text{CO})_6\text{N}_3]^-$, $[\text{Re}(\text{CO})_3\text{N}_3\text{NCO}]^-$, depending on the temperature and solvent used (338a, 463). Carboxyazide (CON_3) derivatives [e.g., Eq. (10)], postulated as intermediates in the

reactions involving nucleophilic attack of azide ions at carbonyl carbon atoms, were discussed in Section III,C together with the reactions of azido complexes with carbon monoxide which form isocyanates and isocyanato complexes. Related reactions of coordinated azido groups with nitriles produced coordinated substituted tetrazole groups (47).

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Infrared Intensities of Metal Carbonyl Stretching Vibrations

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I. Introduction	199
II. Theory	201
III. Measurement	204
A. Method I. Direct Integration	205
B. Method II. An Extension of the Wilson-Wells Method	206
C. Method III. An Extension of Bourgin's Method	207
IV. Bonding	208
V. Solvents	211
VI. The Cotton-Kraihanzel Method	213
VII. The Method of Local Oscillating Dipoles	214
VIII. Bond Angles.	216
IX. CKM and Intensities	218
X. Absolute Integrated Intensities	222
XI. Conclusion	232
References	233

I

INTRODUCTION¹

Early in the development of the chemistry of the metal carbonyls and their derivatives, Cotton *et al.* (42) concluded that the number of infrared-active carbonyl stretching vibrations of a complex is determined by the idealized local symmetry of the terminal carbonyl groups. Although exceptions to this generalization are to be found (50, 60, 117, 134), its utility is now widespread (5, 17, 60, 116, 119). A consequence of this generalization is that the isomeric form of a complex may be determined

¹ For general review articles on infrared band intensities see Brown (29a), Gribov and Smirnov (65a), Overend (113a), Seshadri and Jones (125), and Steele (125a).

from the number of bands observed in its infrared spectra in the 2000 cm^{-1} region. This application stimulated an interest among preparative chemists in the significance of the details of carbonyl stretching frequencies. It was, therefore, only a matter of time before attempts were made to correlate the variations in such spectra with electronic factors for homologous series of complexes.

Before it is possible to interpret on a rigorous basis the behavior of the carbonyl stretching frequencies of a series of isostructural and isoelectronic complexes complete vibrational analyses are necessary. However, it is only within the last few years that far-infrared (137) and laser Raman (84) spectrometers have become available generally. Hence, in the general absence of the data they have provided, earlier complete analyses were limited to the spectra of simple metal carbonyls (for which such information was available). Even for these complexes, the number of force constants exceeds the number of observable frequencies, and model force fields had to be used. Since Urey-Bradley type force fields proved to be unsuitable for carbonyl complexes (86, 105, 106), Jones (80-82) developed a resonance interaction valence force field which reduced the number of force constants by interrelating several on the basis of orbital overlap. This approach is not readily adaptable to less symmetrical substituted carbonyl complexes. Alternative models had, therefore, to be investigated.

Neglecting electronic interactions among the different bond sets to reduce the number of force constants, Bigorgne (17, 18, 99) took into account only mechanical coupling among the various oscillators. However, this method did not receive much attention, presumably because the currently accepted views of the bonding in carbonyl derivatives (1, 20) appeared to be at variance with the assumptions upon which it was based.

Using a simpler approach which elaborated upon earlier proposals (42), Cotton and Kraihanzel (39, 41, 95) assumed that the carbonyl oscillators could be factored out both electronically and mechanically from all other molecular vibrations, and that only electronic coupling among the individual carbonyl bonds need be considered. In addition, they introduced relationships, similar in origin to those proposed by Jones (80, 82), in order to reduce the number of carbonyl bond stretching force constants. Because of its simplicity and qualitative success, the Cotton-Kraihanzel method (CKM) has been applied widely, but it has also been the subject of some controversy (22, 24, 40, 43-45, 78, 79, 83). What is beyond dispute, however, is that its use has brought to the attention of the chemist the variations in, and possible

use of, both relative and absolute intensities of carbonyl stretching vibrations (2, 20, 26, 30, 52, 53, 77, 103, 136).

Immediately preceding the presentation of the CKM, Orgel (111) described a method of correlating the isomeric species with the band assignments and intensities of the terminal carbonyl vibrations of $[L_xM(CO)_{6-x}]$ complexes. Concurrently, El-Sayed and Kaesz (59) presented similar arguments to explain the observed carbonyl stretching frequencies of a series of pentacarbonyl metal halides. The method fired the enthusiasm of the preparative chemist and has been applied to the analysis of the terminal carbonyl stretching vibrations of complexes of a wide range of molecular geometries, meeting with varying degrees of success. What is not generally appreciated, however, is that the essential elements of this approach were given much earlier (42). In the same article the necessary assumptions and algebra for calculating the angle between a carbonyl group and the principal molecular symmetry axis from relative band intensity data were outlined. However, it was not until Beck *et al.* (12, 13) demonstrated its usefulness that the procedure regained attention.

Finally, although Noack (109) pioneered the use of the absolute intensities of carbonyl stretching vibrations for structural information as far back as 1962, the results of very few studies have appeared subsequently. The primary purpose of this article is to attempt to assess the relevance of both relative and absolute intensities of metal carbonyl infrared-active stretching vibrations to structural problems which are known to be characteristic of metal carbonyl chemistry. Although the study of absolute intensities is still beset with practical and theoretical difficulties, these are due, at least in part, to the lack of activity in this field of research. It is hoped, therefore, that this article will help to stimulate a greater interest in the topic.

II

THEORY

The intensity of a fundamental infrared absorption band is given by the equation (135)

$$\int \alpha_\nu(I) d\nu = [N\pi/3c][(\partial\mu/\partial Q_I)_0]^2 \quad (1)$$

Here, $\alpha_\nu(I)$ is the integrated absorption coefficient of the band corresponding to the I th normal mode Q_I at frequency ν , and the integral spans the complete vibration-rotation band. The left-hand side of this equation represents

an observable quantity and embodies the well-known exponential law of absorption. N is the number of molecules per unit volume of sample, and c is the velocity of light. The vector μ is the molecular dipole moment, and $(\partial\mu/\partial Q_I)_0$ is its rate of change with respect to change in Q_I . The quantity $(\partial\mu/\partial Q_I)_0$ is evaluated at the molecular equilibrium configuration. The derivation of Eq. (1) assumes that the molecular dipole moment can be expanded as a Taylor series in terms of nuclear displacements

$$\mu = \mu_0 + \sum_I (\partial\mu/\partial Q_I)_0 Q_I + \text{higher terms} \quad (2)$$

and all but the first derivatives can be neglected. This assumption of electrical harmonicity is only a first approximation since combination and overtone bands are observed for most molecules. However, their intensities are generally much less than those of the corresponding fundamentals. To interpret the right-hand side of Eq. (1), one must set up a model and investigate the resulting description of the dipole moment of the molecule.

Because the coordinate Q_I is a normal coordinate of the molecule, it is conceptually difficult to appreciate the significance of the values of the derivatives $(\partial\mu/\partial Q_I)_0$ obtained from Eq. (1). However, the normal coordinates can be expressed more simply as linear combinations of molecular symmetry coordinates S_J (135).

$$Q_I = \sum_J L_{IJ}^{-1} S_J \quad (3)$$

The coefficients L_{IJ}^{-1} are obtained from the molecular geometry, the masses of the atoms, and the potential energy function of the molecule (135). That is, provided one can carry out a suitable vibrational analysis, it is possible to use Eq. (3) to relate the observed intensities to the dipole moment changes consequent upon alteration of bond lengths or angles. Molecular geometries can be independently determined. In favorable cases, where detailed structural data are not available, molecular geometries may be guessed with some accuracy. Atomic masses are accurately known. The real difficulty concerns the force constants, in terms of which the molecular potential energy function is expressed, and which constitute the unknowns in a vibrational problem. Unfortunately, most molecules have more force constants than frequencies, and their complete potential function cannot be determined. To overcome this problem, one can assume that some of the force constants can be neglected, carry some over from other molecules, or adopt a model force field which reduces the number of distinct force

constants by postulating that some symmetry-unrelated force constants have related values (usually a simple proportion). The form of the force field commonly presents, therefore, a necessary assumption in an interpretation of the intensities of infrared absorption bands in terms of bond properties.

Given a judicious choice of force field, another persistent problem exists. From Eq. (3), one obtains the relationship

$$(\partial\mu/\partial S_J) = \sum_I L_{IJ}^{-1}(\partial\mu/\partial Q_I) \quad (4)$$

in which, as is evident from Eq. (1), the sign of each derivative is indeterminate. However, all of the available choices are not, in general, physically acceptable. Consequently, when the number of coordinates is small one can reasonably hope to arrive at unambiguous conclusions regarding the signs of the various terms. Such circumstances frequently arise for carbonyl stretching vibrations.

If one can reduce the derivatives $(\partial\mu/\partial S_J)$ of Eq. (4) to those characteristic of individual bonds, one can convert the data on many molecules to a common basis. This simplifies considerably the task of relating band intensities to chemical constitution. However, to accomplish this, it is necessary to make the following two assumptions (46, 71):

(1) When a bond is stretched by a length δR , a moment $(\partial\mu/\partial R)\delta R$ is produced, which lies in the direction of the bond.

(2) When one bond is stretched, no moments are produced in other bonds. In other words, the total moment resulting from the simultaneous displacement of several bonds is assumed to be the vector sum of the moments produced by each individual bond. Since the molecular symmetry coordinates are linear combinations of internal bond coordinates R_K (135),

$$S_J = \sum_K U_{JK} R_K \quad (5)$$

one can evaluate, using the observed intensities, bond dipole moment derivatives of the form $(\partial\mu/\partial R_K)$, where, using Eq. (1)–(5),

$$(\partial\mu/\partial R_K) = \sum_I \sum_J L_{IJ}^{-1} U_{JK} (\partial\mu/\partial Q_I) \quad (6)$$

Generally, the number of observed bands exceeds the number of symmetry-distinct bond derivatives, and assumptions (1) and (2) can be tested by calculating the same bond derivatives from the intensities of different bands.

(Since, in this article, we shall only be interested in bond stretching vibrations, the formal extension of these arguments to bond bending coordinates is not included.)

III MEASUREMENT

Assuming that the Beer-Lambert exponential absorption law,

$$I_\nu/I_{0\nu} = (I/I_0)_\nu = \exp -\alpha_\nu cl \quad (7)$$

holds for dilute solutions, the true integrated intensity of an absorption band (A) is defined as

$$A = \int \alpha_\nu d\nu = [I/cl] \int \log_e (I_0/I)_\nu d\nu \quad (8)$$

where the integral spans the limits of the absorption band. $I_{0\nu}$ and I_ν are the incident and transmitted intensities of monochromatic radiation of frequency ν ; c is the concentration of solute in moles per liter; l is the cell path length in centimeters and α_ν is as defined previously.

Because of the use of finite slit widths, the radiation is not monochromatic (and covers an appreciable part of the band envelope) and the measured quantity is an apparent integrated absorption intensity (B),

$$B = [I/cl] \int \log_e (T_0/T)_\nu d\nu \quad (9)$$

where $T_{0\nu}$ and T_ν are the corresponding apparent intensities. The use of finite slit widths, therefore, presents an obstacle to the measurement of true intensities of absorption bands. To investigate the effect of slit width upon the intensities, one must have a detailed knowledge of the true band shape. It has been shown from theoretical considerations (125) that the band contour of broad bands associated with the infrared spectra of liquid-phase systems is determined primarily by collision processes. It follows that a band profile approximating closely to a Lorentzian curve will be observed, so that the expression for the true intensity will be of the form

$$\log_e (I_0/I)_\nu = a/[(\nu - \nu_0)^2 + b^2] \quad (10)$$

where ν_0 is the frequency of the band center, and a and b are constants.

Assuming the true absorptions to have Lorentzian form and assuming a triangular slit function, Ramsay (121, 122) investigated the effect of finite resolving power upon these band shapes for the vibrations of a variety of compounds. This approach reproduced satisfactorily the observed band profiles. However, he did not obtain a simple relationship between true and apparent integrated intensities. Ramsay found that bands are best characterized by their apparent peak intensities $[\log_e(T_0/T)_{\nu_{\max}}]$ and their apparent half-intensity band widths $\Delta\nu_{1/2}^a$. These quantities are related to the true peak intensities $[\log_e(I_0/I)_{\nu_{\max}}]$, the true half-intensity band widths $\Delta\nu_{1/2}^t$ and the slit widths. For ease of reference, the ratios $\Delta\nu_{1/2}^t/\Delta\nu_{1/2}^a$ and $[\log_e(I_0/I)_{\nu_{\max}}]/[\log_e(T_0/T)_{\nu_{\max}}]$ were calculated as functions of the apparent peak intensity and of the ratio of the slit width to the apparent half-intensity band width $\Delta\nu_{1/2}^a$. The data were presented in a tabular form.

Having established both a probable mathematical form of the true shape of an infrared absorption band and its relationship to its apparent or observed profile, Ramsay outlined three methods for determining true integrated absorption intensities. As these methods have been used exclusively in all reported studies of absolute intensities of metal carbonyl stretching vibrations, they are now described in some detail.²

A. Method 1. Direct Integration

From Eqs. (8) and (10), for a solute band in dilute solution obeying the Beer-Lambert law, the area under a Lorentzian band will be given by

$$A = \left[\frac{I}{cl} \right] \int \frac{a}{[(\nu - \nu_0)^2 + b^2]} d\nu = \left[\frac{I}{cl} \right] \left[\frac{\pi a}{b} \right] \quad (11)$$

Using the peak intensity of the band,

$$\log_e(I_0/I)_{\nu_{\max}} = a/b^2$$

and the half-intensity band width $\Delta\nu_{1/2}^t = 2b$, Eq. (11) becomes

$$A = [\frac{1}{2}\pi] [1/cl] \log_e(I_0/I)_{\nu_{\max}} \Delta\nu_{1/2}^t \quad (12)$$

Rewriting directly in terms of observable quantities, Eq. (12) leads to the relationship

$$A = [K/cl] \log_e(T_0/T)_{\nu_{\max}} \Delta\nu_{1/2}^a \quad (13)$$

² For more detailed surveys of the various available methods see the footnote on page 199.

where

$$K = \frac{[\frac{1}{2}\pi][\log_e(I_0/I)_{\nu_{\max}}]}{[\log_e(T_0/T)_{\nu_{\max}}][\Delta\nu'_{1/2}/\Delta\nu''_{1/2}]} \quad (14)$$

Since the two ratios of the right-hand side of Eq. (14) have been tabulated, it is easy to present K in the same form so that by measuring the apparent peak intensity and the apparent half-intensity band width of an absorption band and consulting the relevant tables, the true integrated absorption intensity can be calculated from Eq. (13).

B. Method II. An Extension of the Wilson-Wells Method

Again assuming both a Lorentzian form for the true band shape, and a triangular slit function, a series of apparent band shapes may be calculated for a fixed value of the ratio $s/\Delta\nu'_{1/2}$ and various values of the true peak intensity. Corrections for the area beneath the band wings may be kept to less than 10% by suitably extending the calculations on either side of the band maximum. If apparent absorption curve areas are measured, and wing corrections applied (see below), the ratios of

$$\int \log_e(T_0/T)_\nu d\nu / \int \log_e(I_0/I)_\nu d\nu$$

when plotted against the apparent peak intensities are found to approximate closely to a straight line with negative slope Θ .

It follows that, by tabulating values of Θ for a range of $s/\Delta\nu'_{1/2}$ between 0.1 and 1.0, the true integrated intensity of an absorption band can be obtained by plotting the apparent integrated absorption intensity measured at several different concentrations or path lengths against the apparent peak intensity and determining the best straight line with intercept A and slope $A\Theta$. This procedure of determining A is more accurate than one based upon the method of least squares unless the latter is such as to place least weight upon measurements of weak bands, for which experimental errors are large.

In practice, the absorption curve is plotted as $[\log_e(T_0/T)_\nu]$ versus ν in cm^{-1} , and the area beneath the band profile over a frequency interval of $\pm(\nu - \nu_0)$ determined. The area is obtained by cutting out the band and weighing it, by use of a planimeter, or by applying Simpson's rule (121). Next, a wing correction is made (see below). The apparent integrated

absorption intensity is then calculated from Eq. (9) and plotted against the apparent peak intensity, and the best straight line found by trial and error.

Alternatively, A can be evaluated from a single measurement using the equation

$$B = A + A\theta \log_e (T_0/T)_{v_{\max}} \quad (15)$$

Wing Corrections

In principle, an integration such as in Eq. (1) should be carried out to an infinite distance from the band maximum. In practice, the area beneath a band is measured to finite limits on either side of the band. These limits, in the absence of overlapping bands, are those at which the experimental error becomes of the same order of magnitude as the apparent intensity. However, as Ramsay's calculations have shown, the residual unmeasured area under the band can be appreciable, because the remaining frequency range can be very large although the absorption is small. Correction terms, expressed as percentage of the measured band area, are available for a series of values of the characteristic band quantity $(\nu - \nu_0)/b$. For details, the reader is referred to the original article (121).

C. Method III. An Extension of Bourgin's Method

The area A' under the absorption curve, expressed in terms of fractional absorption, is

$$A' = \int [I - (I/I_0)_v] dv \quad (16)$$

From Eq. (7), one obtains upon expansion

$$A' = \int \left[\alpha_v - \left(\alpha_v \frac{2}{2!} \right) cl + \left(\alpha_v \frac{3}{3!} \right) (cl)^2 - \dots \right] dv \quad (17)$$

or

$$A' = \int \alpha_v [I - F(\alpha_v, c, l)] dv = A - \int F(\alpha_v, c, l) dv \quad (18)$$

and

$$\begin{matrix} A' & \rightarrow & A \\ cl \rightarrow 0 \end{matrix} \quad (19)$$

It has been shown that a plot of the true peak intensity versus $[A(cl)/A']$ is essentially linear, provided that I/I_0 does not exceed 0.8. The most convenient way to obtain A is, therefore, from Eq. (20).

$$A = \phi A' / cl \quad (20)$$

Here, ϕ is a function of the true peak intensity, which has been tabulated for a range of values of $[\log_e(I_0/I)_{\nu_{\max}}]$.

If a spectrometer with a linear wavelength scale is used, the experimental absorption curve has to be replotted as fractional absorption $(T_0 - T)/T_0$ against ν in cm^{-1} , and the area under the band for a range $\pm(\nu - \nu_0)$ determined. A correction for the band wings is applied to obtain A' , and then the true integrated absorption intensity is calculated from Eq. (20). Wing corrections are presented in tabular form in terms of the quantity $(\nu - \nu_0)/b$ and are to be found in the original paper (121).

In all three methods, the assumptions of a Lorentzian band profile and of a triangular slit function were made. However, since Methods II and III involve measurement over the complete experimental curve, whereas Method I uses only three points of this curve, the latter is the most sensitive to the first assumption. Method II depends upon fairly small corrections related to the band shape and the slit function. Method III is almost insensitive to the form of the slit function, but is much more strongly dependent upon the assumed band shape. Consequently, for partially overlapping bands, and in general, Methods II and III are to be preferred, although Method III has speed in its favor.

Finally some general, practical, but simple, points are well worth attention for studies of transition metal carbonyl derivatives. For optimizing the accuracy of absolute integrated intensities, great care must be taken to minimize errors arising from weighing of the sample, from sample and solvent impurities, and from solvent evaporation.

IV BONDING

Before discussing the particular relevance of the preceding sections to carbonyl stretching vibrations, it is necessary to summarize a simplified description of the bonding between a terminal carbonyl group and a transition metal atom, and to consider its sensitivity towards replacement of other carbonyl groups by different ligands.

In carbon monoxide, s - p mixed orbitals from both the carbon and oxygen atoms combine to form the carbonyl group σ -bonding orbital, leaving an outward-pointing s - p mixed orbital on oxygen and another on carbon.

These two orbitals are each occupied, giving lone pairs of electrons that are essentially atomic in character. Two mutually perpendicular, filled, π -bonding orbitals complete the bonding system of the carbon monoxide molecule. When coordinated to a metal it is the less electronegative atom, carbon, which donates lone-pair electron density to a σ -oriented metal orbital. However, from its general chemistry, it is apparent that the donor properties of carbon monoxide are very slight. It is therefore believed that additional π -bonding, in which filled metal orbitals back-donate electron density to the available π^* -orbitals of the carbonyl group, makes a significant contribution to the molecular stability.

For a transition metal complex, equal occupation of the two π^* -orbitals of the carbonyl group is required when its local symmetry within the complex is C_3 or higher. This is the case for carbonyl groups of highly symmetrical molecules such as hexacarbonylchromium or tetracarbonylnickel, and also for axial carbonyl groups of derivatives like $\text{CH}_3\text{Mn}(\text{CO})_5$ and $\text{CH}_3\text{Co}(\text{CO})_4$. It is not, however, a general requirement that this be the case in sets of carbonyl groups which are radially disposed around the principal molecular symmetry axis. A manifestation of such an inequality might be the nonlinearity of the metal-carbon-oxygen skeletons (88, 89). However, since these skeletons are found to deviate by only about 5° for a wide variety of systems, the foregoing description of the bonding of a bound terminal carbonyl group can be taken to be sufficient for the present purposes. A note of caution is appropriate, however. This asymmetry seems to be an important factor in determining the intensity of Raman bands (93).

Calculations using Slater atomic orbitals indicate that relatively little change in σ -electron density occurs during a small vibration of carbon monoxide, but that there are quite large changes of the π -electron density (90). It may be concluded, therefore, that π -bonding effects probably dominate the changes of repulsive and attractive forces within a bound vibrating carbonyl group. A rider to this is that, for a vibrating carbonyl group, the lone pair of electrons located, essentially, on the oxygen atom remains little altered.

There are several consequences of the above qualitative discussion. First, while the symmetry of the isolated CO molecule is $C_{\infty v}$, on coordination this commonly drops to C_s . Since the local symmetry is always maintained during a bond stretching vibration, mixing of the in-plane with the out-of-plane (π) orbitals cannot occur during a CO bond stretching vibration. Secondly, the *relative* charge densities on the atoms in a coordinated

carbon monoxide group appear to be $\delta^+O-C\delta^-$ [as indicated by *ab initio* calculations on $Ni(CO)_4$, which also suggest that both C and O atoms carry small residual negative charges] (138). Stretching the bond of a coordinated CO group most probably leads to a transfer of electron density $C \rightarrow O$ (30). If this transfer occurs and is located in the π -system (as the overlap arguments above lead us to expect) then the "empty" π^* -orbitals of the CO group are lowered in energy and increasingly localized on the carbon atom as the CO bond is stretched. Both features lead one to expect enhanced $M \rightarrow C$ π -electron donation (i.e., bonding). This argument may be usefully inverted. Suppose one replaces CO groups attached to a metal by ligands of greater σ -donor but poorer π -acceptor ability. An immediate consequence will be a decrease in the effective nuclear charge of the metal atom, so that the metal d -orbital energy and size both rise. These two factors will lead to an enhancement of the $M-C$ π -bonding for the remaining CO ligands with a consequent weakening of the CO bond, which will be reflected in a smaller bond stretching force constant. Empirically, it is found that progressive substitution of carbonyl groups in, for example, hexacarbonylchromium can be followed by monitoring the concomitant decreasing carbonyl stretching frequencies.

Using parallel arguments, it can be reasoned that the presence of either highly electronegative groups (such as a halogen atom) within the complex and/or an increased effective nuclear charge on the metal atom will lead to increased carbonyl stretching frequencies relative to those of a parent complex. These conclusions are backed by a wealth of experimental data (1, 6) and can be used with reasonable confidence as a basis for the discussion of the significance of the intensities of metal carbonyl stretching vibrations.

Coulson (31, 46) has outlined several theoretical reasons why a rigorous division of the molecular dipole moment derivative into fixed bond contributions cannot be generally anticipated (55, 56). They call into question the use of some of the assumptions made in Section II. Their relevance to carbonyl stretching vibrations must be considered, and we shall now do this in terms of the naive bonding scheme discussed above.

The valence-shell electron densities may be divided into two classes. First there is that electron density which is associated with orbitals which are, primarily, involved in the molecular bonding. Secondly, there is that electron density which is associated with nonbonding orbitals, and which may often be regarded as composed of "lone pairs."

When a molecule or ligand possesses such a lone-pair orbital, it is evident

that a local dipole moment will, in general, be associated with it. Since such a moment is primarily atomic in origin it is referred to as an atomic dipole. Dipoles of this type are known to be quite large for molecules such as ammonia and water (31). However, we have already concluded that the atomic dipole on the oxygen atom of a bonded carbonyl group remains essentially unaltered when the CO bond length changes. If this is so, the corresponding derivative of the atomic dipole will probably be very small. Even if it were large, the change adds vectorially to the bond derivative (with which it is colinear) to give a resultant dipole moment derivative the properties of which are in a 1:1 correspondence with those of a bond dipole moment derivative. We conclude that the presence of lone pairs does not unduly complicate the interpretation of the intensities of CO stretching vibrations.

Further, stretching a terminal carbonyl group preserves the local symmetry of that group, and we have assumed that only changes in π -overlap result. We have seen that the out-of-plane π -orbital preserves its identity under such a stretch but it is not necessary that the same be true of the corresponding in-plane orbital. This orbital has the same symmetry characteristics as the C—O σ -orbitals and a slight mixing between them might be anticipated. If we assume that such mixing is negligible then the possibility of orbital bond following (and the induction of a derived component transverse to the CO bond axis) is eliminated.

Finally, it is recognized that extensive delocalization of π -electron density occurs within these molecules. This implies that models based upon a simple bond additivity are not strictly valid. A rigorous description of such systems must include terms of the form $(\partial\mu_f/\partial R_j)$, which relate to interaction processes among the individual bonds. Apparently, this criticism remains and its severity can only be assessed from the internal consistency of theories in which it is neglected.

V

SOLVENTS

In general, the position, shape, and intensity of an infrared-active absorption band are solvent-sensitive. In particular, carbonyl stretching vibrations of metal carbonyl complexes exhibit large frequency shifts (10, 11, 21, 27, 28, 37, 64, 69, 72, 115, 120) and sizable broadening of bands

(11, 21, 115, 116). However, no detailed studies have appeared which correlate variations of absolute intensities with solvent.

From the available data on frequency shifts several general trends have been established. Frequency shifts relative to a given standard solvent such as *n*-hexane or cyclohexane are greater for asymmetric vibrations than the corresponding symmetric vibrations. For a particular complex, frequency shifts increase with the polarity of the solvent and the lower the frequency in the reference solvent the greater is the observed shift. Increased substitution of the parent complex by ligands of predominantly enhanced σ -donor character leads to increased frequency shifts. When discussing the influence of solvent upon the internal vibrations of a solute, two types of model are commonly considered. The solvent molecules can be considered as a continuous medium with the solute molecules occupying a set of cavities in the solvent. Alternatively, specific interactions can be assumed to persist among solvent and solute molecules forming a discontinuous medium. Although very little is known about the detailed nature of such specific interactions, it is necessary to assume their existence in order to present a coherent description of the observations. It has been assumed that the solvent molecules interact with the dipoles of the various carbonyl groups and thus induce a redistribution of the $d_{\pi}-p_{\pi}$ electron density within the complexes. However, halide complexes appear to be in a separate class in that increased vibrational energies are observed (10, 11, 69). This is normally attributed to specific interactions occurring among the solvent molecules and the available dipoles on the halogen atoms.

Since specific interactions cannot be ignored, at least for the more polar solvents, it is improbable that all of the solute molecules in a particular solvent have an identical environment. Only if the vibrational frequencies appropriate to the various species present in solution differ appreciably will they be resolved. If, as is generally the case for carbonyl stretching vibrations, they cannot be resolved, broadening of the bands occurs. The true shape of the band is, therefore, no longer Lorentzian but has acquired some characteristics of a Gaussian error curve. Obviously, the greater the broadening the greater will be the Gaussian component and hence the less adequate the use of Ramsay's method. There is no evident reason why the various vibrations of a particular molecule will show the same solvent dependence. In consequence, especially for the more polar solvents, this could result in the calculation of different bond dipole moment derivatives from the various vibrational symmetry species (see Section IX). It seems

preferable, therefore, to restrict the use of Ramsay's methods to measurements made in nonpolar solvents wherein specific interactions are presumably minimized.

VI

THE COTTON-KRAIHANZEL METHOD

Since most the available data on both relative and absolute intensities of metal carbonyl stretching vibrations have been discussed in terms of the CKM, (20, 39, 41, 95), or modified forms of it, we now give a brief outline of this model.

Assuming electrical coupling but no mechanical coupling between any two carbonyl oscillators, i.e., assuming the heavy transition metal atoms remain at rest during carbonyl stretching vibrations, the general form of the secular equation

$$|\mathbf{F} - \lambda \mathbf{G}^{-1}| = 0$$

becomes

$$|\mathbf{F} - (\lambda/\bar{m})\mathbf{E}| = 0 \quad (21)$$

where \bar{m} is the reciprocal of the reduced mass of the carbonyl group.³ The \mathbf{F} matrix is generated in the normal way (135) from the relationship

$$\mathbf{F} = \mathbf{U}\mathbf{f}\mathbf{U}'$$

where \mathbf{U} is, as before, a real unitary or orthogonal transformation matrix defined by the transformation from internal coordinates to symmetry coordinates. The \mathbf{f} matrix is defined by the force field. In this case its elements are bond stretching force constants and bond stretching interaction constants only. The number of interaction constants is reduced by interrelating them on the basis of elementary bonding considerations. Two *trans*-carbonyl groups of a complex having an octahedral ligand distribution π -bond to the same two d_{π} metal orbitals of the central metal atom but two *cis*-carbonyl groups share only one d_{π} orbital. Since π -bonding effects probably dominate the changes of repulsive and attractive forces of a bound terminal carbonyl group (see Section IV), it would appear a reasonable approximation to assume that all interaction constants between *cis*-carbonyl

³ To avoid confusion with the dipole moment terms we do not use the usual symbol for reduced mass.

groups within one molecule are equivalent and that they are half the magnitude of *trans*-carbonyl group interaction constants. With these assumptions as a starting point it is possible to make band assignments by imposing the further restriction that all interaction constants must be positive. This additional condition also emerges from the preceding bonding arguments.

Although the model was originally proposed for octahedral complexes, it has been applied in modified forms to other molecular geometries (20, 39, 48). In general it has been used, with a reasonable degree of success, for band assignments, although its limitations, and even its validity, have been discussed (Section I).

VII

THE METHOD OF LOCAL OSCILLATING DIPOLES

From Eqs. (4), (5), and (8) (Section II), the resultant dipole moment derivative for the normal coordinate Q_I is

$$\left(\frac{\partial \mu}{\partial Q_I}\right) = \sum_J \sum_K L_{JI} U_{JK} \left(\frac{\partial \mu}{\partial R_K}\right) \quad (22)$$

and the intensity of the absorption band is proportional to the square of this quantity. If one assumes that the normal coordinates for carbonyl stretching vibrations are identical to the carbonyl symmetry coordinates, the condition $L_{JI} = \delta_{JI}$ holds, and one summation vanishes. Assuming that all carbonyl groups of any particular complex have essentially equivalent bond dipole moment derivatives in addition to the conditions listed in Section II, the various bond derivatives will only differ in their orientations about the central metal atom. Since the matrix elements U_{JK} are readily available, crude relative intensities of the carbonyl stretching vibrations can be obtained easily on this basis by comparing the squares of the appropriate vectorial sums of the bond moment derivatives.

The simplicity and power of this approach, known as the method of local oscillating dipoles, was first demonstrated by Orgel (111), who used it to assign the spectra of octahedral molybdenum carbonyl complexes. Very similar arguments were presented simultaneously, but independently, by El-Sayed and Kaesz (59) in a discussion of the spectra of pentacarbonyl halide derivatives of Group VIIA metals. Subsequently, the model has been applied to the assignment of bands in the spectra of numerous octa-

hedral pentacarbonyl derivatives (2, 3, 15, 36, 38, 47, 50, 65, 70, 76, 124, 126, 127). A rather striking application of this method was its use in inferring not only the transient existence of pentacarbonyls of chromium molybdenum, and tungsten but also their molecular geometries (128, 129).

Although the method was originally used for octahedral complexes and, indeed, has proved of some use for a wide variety of these types of complex (8, 9, 25, 49, 68, 73, 74, 96), it has also been applied to the problems of band assignments in the carbonyl stretching spectra of trigonal bipyramidal complexes of iron (130) and cobalt (20, 23, 48, 66, 67, 117, 118), albeit with less success. This approach has also been extended to binuclear carbonyl complexes (4, 51, 58, 62, 63, 100, 101, 112, 113) and even to trinuclear complexes (75), but, in general, it becomes severely limited in its utility. There are several reasons for this. Clearly, when bands are strongly overlapping, the intensity distribution of a band (i.e., peak shape) is as important as its integrated intensity, so that an approach which neglects the former will be of little value (131). Moreover, the method is based upon the assumption that it is only necessary to consider the idealized local symmetry of the bound carbonyl groups. In practice, although this holds good for the vast majority of complexes, there are a few classes of complex which are now known to be exceptions (50, 117, 134). For such compounds, the model cannot be used. However, the most acute restriction upon the usefulness of the model is the assumption that the normal coordinate can be identified with the symmetry coordinates of the molecule. Where more than one molecular vibration belongs to the same symmetry species and they are of similar energies, appreciable coupling among them usually occurs. Such coupling is accompanied by intensity transfer which precludes the use of the simple method of local oscillating dipoles (Section VIII).

Two extensions of Orgel's method serve to illustrate that it may have yet other applications. It has been demonstrated that although the model is even cruder in its application to solid-state studies of carbonyl stretching vibrations, its use may, nevertheless, give results which are in good qualitative agreement with the findings of more detailed analyses (32-35). Finally, qualitative arguments based upon an extension of Orgel's method have been used successfully to aid in band assignments of carbonyl stretching overtone and combination vibrations of metal carbonyl complexes (54, 97, 98). More recently, these arguments have been formalized and applied with a reasonable degree of success to the assignment of binary absorptions of a wide variety of metal carbonyl complexes (91).

VIII BOND ANGLES

From Eq. (22) (Section VII), it follows, assuming that molecular symmetry and normal coordinates can be equated, that

$$\left(\frac{\partial\mu}{\partial Q_I}\right) = \sum_K U_{IK} \left(\frac{\partial\mu}{\partial R_K}\right) \quad (23)$$

If the bond coordinate R_K is inclined at the angles θ and α to the molecular X and Z axes, respectively, it can readily be shown that Eq. (23) becomes, for the totally symmetric carbonyl stretching vibration

$$\left(\frac{\partial\mu}{\partial Q_I}\right) = \sum_K U_{IK} \cos \alpha \left(\frac{\partial\mu}{\partial R_K}\right) \quad (24)$$

and for the asymmetric carbonyl stretching vibration which has a resultant dipole moment derivative along the molecular X axis,

$$\left(\frac{\partial\mu}{\partial Q_I}\right)_X = \sum_K U_{IK} \sin \alpha \cos \theta_K \left(\frac{\partial\mu}{\partial R_K}\right) \quad (25)$$

Here $(\partial\mu/\partial R)$ is the bond stretching dipole moment derivative for any one of the carbonyl set. Since the angles θ_K are determined by the molecular symmetry, a knowledge of the relative or absolute intensities of the symmetric and asymmetric vibrations, together with Eqs. (24) and (25), permit the evaluation of the angle, α . Where the asymmetric mode is doubly degenerate, it is necessary, before calculating the angle, to multiply by a factor of 2 the square of the right-hand side of Eq. (25). In general, therefore, the following relationship holds,

$$\frac{A_{\text{asym}}}{A_{\text{sym}}} = \tan^2 \alpha \quad (26)$$

Having determined α , it is possible to calculate the interbond angle δ of the carbonyl groups from the expression,

$$\cos \delta = (1 - 2 \sin^2 \alpha \sin^2 \theta/2) \quad (27)$$

and compare the results with those obtained by X-ray or neutron diffraction studies. Equation (27) holds for C_n ($n > 2$). When $n = 2$, the angles α and δ are identical.

This procedure was first outlined by Beck *et al.* (12, 13), who used it to provide a very simple but elegant demonstration of the utility of the method of localized oscillating dipoles. From the relative intensities, and in some cases the absolute intensities, of a variety of carbonyl complexes, the interbond angles between symmetry-equivalent carbonyl groups were calculated and were in good agreement with those determined from structural studies. Subsequently, the method has been tested successfully using absolute intensities (16, 19, 32) but the complexes investigated were such that there was no possibility of coupling between stretching vibrations. Analyses of the data obtained for a variety of systems containing symmetry-nonrelated carbonyl groups have shown that the simple approach is inadequate and that allowance must be made for coupling (20, 26, 53, 77, 103, 136), a result which was to be expected (Section VII). However, these more detailed studies prompted the discussion of some interesting aspects of intensity transfer among carbonyl absorptions (57, 92, 104). The complicating effects of coupling have not always been recognized but may not always be important. For example, calculation of the interbond angle between the carbonyl groups of *tris*(trifluorophosphine)iron(0) dicarbonyl, $[(PF_3)_3Fe(CO)_2]$, from the observed relative intensities of the carbonyl stretching vibrations has been cited as evidence that the molecule has a trigonal bipyramidal structure with two equatorial carbonyl groups (132). The value calculated for α is much greater than 90° and, therefore, it was concluded that an axial substituent is improbable (two axial substituents would lead to only one infrared absorption). Similar reasoning has been applied to other dicarbonyl complexes (114, 133). Although the possibility of coupling was not discussed by the original authors, it is not difficult to show that, within the present context, two carbonyl groups at right angles to each other give two infrared peaks of equal intensity irrespective of the amount of coupling between them.

Another criticism which may be made of the calculations of bond angles from relative intensities is the significance of the dependence of these intensities upon the choice of solvent (27). The importance of this point emerged upon comparison of the results of two laboratories (13, 27), the disparities between which could be due to inherent experimental errors (Section III) and/or solvent effects (Section V). A very marked solvent dependence of intensities was found.

The general success of the method of calculating intercarbonyl bond angles from relative intensity data is in large measure due to the fact that

carbonyl modes are essentially uncoupled from the other molecular vibrations. However, two extensions of the method to situations in which this condition does not persist have been reported recently. Firstly, interbond angles of the three metal atoms of complexes of the type $X_2Sn[Co(CO)_4]_2$ have been calculated from metal-metal vibrational intensity data. Variation of the angle within the series correlates qualitatively with the electronegativity of the substituent group X, although the calculated angles were not, in themselves, assumed to be significant (117). Secondly, for a series of derivatives of the type $CpFe(CO)_2X$ and another of the type $CpMo(CO)_2L$, the relative intensities of what were held to be essentially $M-C-O$ bonding vibrations were used as an aid to band assignments (102). The relative intensity of the bands corresponding to the two in-plane $M-C-O$ bonding coordinates are related to the $OC-M-CO$ angle and, assuming a reasonable value for the latter, can be assigned on the basis of their relative intensities.

As a further extension of the method, the interbond angle of the carbonyl groups of derivatives of the type $CpFe(CO)_2X$ have been calculated by extending the method of oscillating dipoles to the second derivative of the carbonyl bond dipole moment (91). The results obtained are in remarkable agreement with those calculated using the absolute intensities of the fundamental carbonyl stretching vibrations (52).

IX

CKM AND INTENSITIES

Since Eq. (23), (24), and (25) are invalid for the normal coordinates of molecules having more than one carbonyl stretching vibration of the same symmetry species, Eq. (22) has to be used and Eq. (24) is replaced by

$$\frac{\partial \mu}{\partial Q_I} = \sum_J \sum_K L_{JI} U_{JK} \cos \alpha \left(\frac{\partial \mu}{\partial R} \right) \quad (28)$$

Here, the terms L_{JI} are elements of the **L** matrix which diagonalizes the **F** matrix (135),

$$\mathbf{L}'\mathbf{F}\mathbf{L} = \mathbf{\Lambda} \quad (29)$$

and also has the property (135),

$$\mathbf{L}'\mathbf{G}^{-1}\mathbf{L} = \mathbf{E} \quad (30)$$

In Eq. (29), \mathbf{A} represents the matrix containing $\lambda (=4\pi^2c^2\nu_i^2)$ values along its diagonal, and, in Eq. (30), \mathbf{E} represents the unit matrix. From Eq. (29) it is evident that the elements L_{JI} are dependent upon the force and interaction constants and thus upon the details of the assumed force field. In general, then, to interpret the relative or absolute intensities of carbonyl stretching vibrations, it is necessary first to assume some model force field and then evaluate the elements of the \mathbf{L} matrix.

Alternatively, observed relative intensities of some tetracarbonyl metal complexes may be used as an additional source of information for the evaluation of force and interaction constants of a modified CKM (20, 48). Bor (20) used the observed intensity ratios of the two a_1 modes of the derivatives HCo(CO)_4 , $\text{CH}_3\text{Co(CO)}_4$, and $(\text{C}_6\text{H}_5)_3\text{PFe(CO)}_4$ (all of which have, essentially, trigonal bipyramidal structures) to obtain the most probable range of force and interaction constants for these complexes, assuming a modified CKM field. Independently, the observed relative intensities of a series of complexes of the type $\text{R}_3\text{MCo(CO)}_4$ ($\text{M} = \text{Si, Ge, Sn, Pb}$; $\text{R} = \text{Cl, Br, I, CH}_3, \text{C}_2\text{H}_5, \text{and CH}_3\text{O}$) were cited as evidence for approximately maximum coupling between the two a_1 modes (48). This assumption enabled the calculation of the requisite force and interaction constants of the CKM. The results obtained were in good agreement with those of Bor (20).

Manning and Miller (103) were the first to use the matrix elements derived from a force constant analysis in the interpretation of the relative intensities of bands of which more than one are of the same symmetry species. They examined, with the aid of the CKM, the coupling of the two a_1 modes of some pentacarbonyl manganese(I) derivatives, a series which has since been the subject of considerable research. For normal coordinates of the same symmetry (i.e., expressible as linear combinations of two symmetry coordinates), it should be noted from Eq. (28) that their associated resultant dipole moment derivatives can have one of two values dependent upon the choice of signs of the L_{JI} elements. That is, one does not know, *a priori*, which band corresponds to the symmetric and which to the antisymmetric combination of the two symmetry coordinates. Corresponding to each of the two alternatives there will be calculated different values of α . However, since the angle α is frequently known at least approximately, the correct choice of sign of \mathbf{L} matrix elements for each normal mode can usually be determined. This is a situation which occurs for the two a_1 carbonyl stretching modes of pentacarbonyl metal derivatives. (26, 53, 77, 87).

Manning and Miller (103) found that the relative intensities of these

vibrations could not be explained by vibrational coupling alone. From Eq. (28) it can be seen that small variations of the angle α will produce sizable changes in the intensity of the a_1 mode, when α is close to 90° . The data were interpreted, therefore, on the basis of both coupling and deviations of the angle α from 90° . Later, Wing and Crocker (136) discussed the absolute integrated intensities of the two b_2 modes of decacarbonyl dimers [these modes are out-of-phase combinations of the a_1 vibrations of the $M(CO)_5$ units] in terms of both coupling and an electrostatic repulsive force between the two halves of the dimers. Allowing for coupling between the (a_1) modes of the $M(CO)_xL_{5-x}$ fragments in $[M(CO)_xL_{5-x}]_2$ species, they calculated the angle α and obtained physically reasonable results.

From Eq. (28) and its counterpart for asymmetric vibrations (Section VIII).

$$\frac{\partial \mu}{\partial Q_I} = \sum_J \sum_K L_{JI} U_{JK} \sin \alpha \cos \theta_K \left(\frac{\partial \mu}{\partial R} \right) \quad (31)$$

it is readily shown, due regard being paid to degeneracy, that the ratio of the total intensity of the two a_1 absorptions to that of the e mode, for penta-carbonyl metal derivatives, has the form

$$\frac{A_{\text{sym}}}{A_{\text{asym}}} = \frac{1 + 4 \cos^2 \alpha}{4 \sin^2 \alpha} \quad (32)$$

Equation (32) is based upon the additional assumptions that transverse derivatives can be neglected (*vide infra*) and that the carbonyl group bond moment derivatives are transferable. This equation was originally presented by Brown and Darensbourg (30), who used it to calculate the angle α for a series of derivatives. The deviations from 90° were so large as to be physically unreasonable and led them to an alternative approach. The explanation they offered was that there is a different characteristic moment derivative for each symmetry mode. It may be noted that an explanation of this type is in keeping with the comment made in Section V concerning solvent effects. Further, contrary to all previous discussions, these authors suggested that the localized dipole moment derivatives involve the whole $M-C-O$ skeleton and, consequently, coupling among the metal-carbon and carbon-oxygen bond stretching vibrations must be accounted for. Again, this goes some way towards meeting the final criticism of Section IV. In a subsequent paper, the same authors investigated the dependence of the ratio of the intensities of the two a_1 modes upon the force field and concluded that the

CKM was adequate (53). Apparently, this conclusion concurs with that of Johnson *et al.* (77), but conflicts with that of Braterman *et al.* (26). However, assuming the CKM holds, a vibronic contribution to the a_1 intensities (29) and the same characteristic dipole moment derivative for the two a_1 modes, Darensbourg and Brown (53) calculated the two characteristic moment derivatives for the symmetric and asymmetric modes and obtained again physically reasonable values of the angle α for a range of pentacarbonyl metal complexes.

Using a refined version of the CKM by incorporating vibrational data from isotopically labeled molecules, Braterman *et al.* (26) calculated the angle α and different bond moment derivatives for symmetry-distinct carbonyl sets from the absolute integrated intensities of some pentacarbonyl metal halides and for decacarbonyl dirhenium(0). Evidence for the possible existence of different bond moment derivatives had been reported earlier (85, 123) but lack of data prevented further investigation at that time (103). The more detailed analysis of Braterman *et al.* although confirming the nontransferability of bond moment derivatives did not, however, remove all ambiguities, since one angle α of 79° was calculated for decacarbonyl dirhenium, whereas the corresponding angle for decacarbonyl dimanganese as determined by X-ray analysis, is 97° . It appeared, therefore, that at least one other factor is involved in the intensities of carbonyl stretching vibrations. While reporting a similar study of $\text{XM}(\text{CO})_5$ derivatives, Johnson *et al.* (77) commented upon an assumption common to all reported studies, that transverse bond moment derivatives could be neglected (Section IV). They cited as justification for this the earlier studies of Beck *et al.* (13, 103). Recently, this has been confirmed by a more detailed analysis (87) which shows that transverse bond moment derivatives make a relatively small contribution (a maximum of about 15% of the bond contribution) to the intensity, so it is improbable that they provide an explanation of the results obtained by Braterman *et al.*

In summary, from the considerable study that has been made of pentacarbonyl metal complexes, there is some doubt about the adequacy of the CKM for the calculation of both relative and absolute intensities (26, 53). Measured intensities obtained from different laboratories lead to differing results (2, 53, 136). Evidence suggests that individual carbonyl bond dipole moments exist (85, 123) and that solvent effects could cause the coexistence of characteristic dipole moment derivatives for the various modes (Section V). In any case, the existence of the latter has, independent of solvent

effects, been claimed (30, 53). Transverse bond moment derivatives can probably be neglected (12, 13, 77, 87), as can cross terms of the form $(\partial\mu_i/\partial R)$, especially when a vibronic contribution is incorporated (53). Despite the various combinations of the foregoing assumptions which have been used, the values of the angle α have almost always been physically reasonable. It seems clear, therefore, that the values calculated for α cannot be used to test the validity of the assumptions made in any particular model. Since these comments can probably be generalized to other molecular types such as *cis*- $L_2M(CO)_4$ and certainly to $LM(CO)_4$, only the most general and consistent trends in absolute integrated intensities can be discussed at present. More detailed analyses must await more systematic studies of, for example, solvent effects.

X

ABSOLUTE INTEGRATED INTENSITIES

In view of the general discussion of Sections VII, VIII, and IX, where it was concluded that coupling was probably the major reason for the failure of the method of localized oscillating dipoles, it seems reasonable to attempt an analysis of the available data wherein coupling among vibrations can be eliminated. In a recent report of the relative intensities of carbonyl stretching vibrations of arene tricarbonyl metal derivatives, Brown and Hughes (27) demonstrated that the total integrated intensities for a set of symmetry-related dipole derivatives were independent of the angle between any of them and the threefold axis, i.e., α (Section VIII). By extending this reasoning to the analyses of pentacarbonyl and tetracarbonyl metal derivatives given by Brown and Darensbourg (30), it follows that the total absolute integrated intensity of any particular molecule is independent both of the angle α and of any vibrational coupling, provided that the bond moment derivatives of all carbonyl groups in a molecule are identical and that there is only electronic interaction between the carbonyl groups. These requirements appear to be, at least approximately, valid for most of the metal carbonyls and their derivatives which have been studied.

As a means of comparing the absolute integrated intensities of the carbonyl stretching vibrations of a wide range of complexes of varying molecular symmetries and of differing numbers of carbonyl groups, Noack (109) used the specific intensity of each compound. This is defined as the intensity

per carbonyl group and is obtained from the total intensity by dividing it by the number of carbonyl groups present in the molecule. Although this parameter is frequently reported along with the absolute integrated intensities of the various bands (2, 16, 19, 52, 108, 109), it is often omitted (12, 14, 30, 53, 61, 94, 107, 136). In Tables I to VII the data reported for a variety of metal carbonyl derivatives have been converted to practical units (2, 125), and the specific intensities included. In Table VIII the conversion factors of some commonly used units of intensity to practical units are given. Most of the subsequent discussion will deal with specific intensities.

It was first pointed out by Noack (109) that metal carbonyl stretching vibrations can be up to 40 times more intense than those of saturated ketones. Explanations for such high intensities have been given in terms of delocalized dipole moment derivatives (Section IV) and in terms of the predominance of π -bonding effects (19, 30). They are based upon arguments closely related to those presented in Section IV. Stretching of the carbonyl bond lowers the energy of the p_{π^*} orbitals which act as acceptors for the metal d_{π} electron density. Charge is, therefore, transferred to the carbonyl groups. It is assumed that smaller effects due to variations in σ -bonding can be ignored. This assumption is in accord with many of the data given in Tables I to VII, the salient features of which will now be considered.

As Beck and Nitzmann (14) observed, the specific intensities of the species $V(CO)_6^-$, $Cr(CO)_6^+$, and $Mn(CO)_6^+$, which are, respectively, 947, 610 and 252×10^{-2} liter mole $^{-1}$ cm $^{-2}$ as measured in tetrahydrofuran, show a rather striking linear dependence upon the formal oxidation state of the control metal atom.⁴ The same trend also occurs for the species $W(CO)_6$ and $Re(CO)_6^+$, and it is taken to indicate the availability of the d_{π} metal electron density. In fact, there is now a considerable body of data available to support the general conclusion that the intensities of the carbonyl stretching vibrations of an isoelectronic and isostructural series of derivatives increase steadily from cations through neutral molecules to anions. For examples, compare the following pairs of species: $Ni(CO)_4$, $Co(CO)_4^-$ (Table I); $M(CO)_5X$, $M'(CO)_5X^-$ (Table II); *cis*- $M(CO)_4X_2$, *cis*- $M'(CO)_4X_2^-$ (Table III); and less rigorously $M_2(CO)_{10}$, $HM_2'(CO)_{10}^-$ (Table VII). Beck and Nitzmann also concluded that the effect on intensities on going from a less polar to a more polar solvent increased from cation

⁴ It appears that the *relative* intensity of the two Raman-active modes for octahedral carbonyl species show a similar dependence on the formal oxidation state of the central metal [S. F. A. Kettle, I. Paul, and P. J. Stamper, *Chem. Commun.* 1724 (1970)].

TABLE I
 ABSOLUTE INTEGRATED INTENSITIES (A) OF METAL CARBONYLS

Compound	Solvent	$A \times 10^{-2}$ [liter mole ⁻¹ cm ⁻²] ^a	Specific intensity ^b	References
Cr(CO) ₆	<i>n</i> -Hexane	2790 (T_{1u})	465	109
	<i>n</i> -Hexane	2765	461	2
	Tetrachloroethylene	3054	509	109
	Carbon tetrachloride	3071	514	14
	Tetrahydrofuran	3661	610	14
Mo(CO) ₆	Cyclohexane	2520	420	16, 19
	<i>n</i> -Hexane	3232	539	2
	<i>n</i> -Hexane	3196	533	30, 77
	<i>n</i> -Hexane	3005	501	109
	Tetrachloroethylene	3111	519	109
W(CO) ₆	<i>n</i> -Hexane	3316	553	109
	<i>n</i> -Hexane	3322	554	2
	Tetrachloroethylene	3220	537	109
	Carbon tetrachloride	3970	662	14
	Tetrahydrofuran	4651	775	14
V(CO) ₆	Dichloromethane	3909	651	14
KV(CO) ₆	Tetrahydrofuran	5681	947	14
Mn(CO) ₅ FeCl ₄	Tetrahydrofuran	1511	252	14
Re(CO) ₅ FeCl ₄	Tetrahydrofuran	1268	211	14
Fe(CO) ₅	Cyclohexane	690 (A''_g)	366	19
		1140 (E')		
		658	346	109
	<i>n</i> -Hexane	1072		
		705	370	109
Ni(CO) ₄	Cyclohexane	1145		
		1040 (T_2)	260	19
		1450	363	109
	Carbon tetrachloride	1390	348	14
	Tetrahydrofuran	1980	495	14
NaCo(CO) ₄	Diethyleneglycol			
	diethylether	3001	750	14
	Pyridine	2120	530	109
Co(CO) ₃ NO	Tetrahydrofuran	139 (A_1)	415	14
		1120 (E)		
NaFe(CO) ₃ NO	Diethyleneglycol diethylether			
		152	516	14
		1429		

^a Absolute integrated intensities given in all tables are in practical units (109, 125), whereas it must be noted that A as defined in the text [Eq. (8)] is the Ramsay and Jones unit. Conversion factors interrelating some of the various commonly used units of intensity to practical units are to be found in Table VIII.

^b Specific intensity as defined by Noack (109).

TABLE II

ABSOLUTE INTEGRATED INTENSITIES OF PENTACARBONYL METAL DERIVATIVES

Compound	Solvent ^a	$A \times 10^{-2}$ [liter mole ⁻¹ cm ⁻²] ^b				Specific intensity	References
		$A_1^{(2)}$	B_1	E	$A_1^{(1)}$		
Mn(CO) ₅ Cl	a	21	—	1034	475	306	2
Mn(CO) ₅ Br	a	44	—	1194	644	376	2
	a	23	—	1099	534	331	30
Mn(CO) ₅ I	a	85	—	1247	781	423	2
	b	66	—	945	—	—	12
Re(CO) ₅ Br	a	24	—	1464	639	425	2
	a	15	—	1442	617	415	30
Re(CO) ₅ I	a	44	—	1408	643	419	2
Mn(CO) ₅ CF ₃	b	15	—	1140	—	—	12
Mn(CO) ₅ CH ₃	b	28	—	1060	—	—	12
Cr(CO) ₅ Cl ⁻	a	25	—	1593	619	447	2
Cr(CO) ₅ Br ⁻	a	31	—	1592	639	452	2
Cr(CO) ₅ I ⁻	a	73	—	2147	918	628	2
W(CO) ₅ Cl ⁻	a	23	—	2190	907	624	2
W(CO) ₅ Br ⁻	a	26	—	2129	887	608	2
W(CO) ₅ I ⁻	a	36	—	2073	990	620	2
Cr(CO) ₅ P(C ₆ H ₅) ₃	c	165	—	—	2462	525	30
Mo(CO) ₅ C ₆ H ₁₀ NH	c	41	—	2484	543	614	53
Mo(CO) ₅ C ₆ H ₅ N	c	52	—	2406	530	598	53
Mo(CO) ₅ P(C ₆ H ₅) ₃	c	171	—	—	2901	614	30
Mo(CO) ₅ As(C ₆ H ₅) ₃	c	151	26	2076	582	567	53
Mo(CO) ₅ Sb(C ₆ H ₅) ₃	c	179	—	—	2710	578	30
Mo(CO) ₅ P(CH ₃ O) ₃	c	90	60	2041	604	559	53
	d	65	70	1540	440	425	16
Mo(CO) ₅ P(C ₂ H ₅ O) ₃	c	80	107	2054	612	571	53
Mo(CO) ₅ P(C ₆ H ₅ O) ₃	c	112	—	—	2458	514	53
Mo(CO) ₅ P							
(OCH ₂ CH ₂) ₃ CC ₂ H ₅	d	60	—	1720	340	424	16
Mo(CO) ₅ PCl ₃	c	143	—	1941	525	522	53
Mo(CO) ₅ P(C ₂ H ₅) ₃	d	80	—	1600	400	415	16

^a a, Chloroform; b, *n*-heptane; c, *n*-hexane; d, cyclohexane.^b Modes defined in reference (2).

through to the isoelectronic anion. This was explained in terms of dipolar interactions with solvent molecules (Section V).

Another observation, which has been consistently reported (2, 14, 27, 108, 109) and is in good agreement with π -bonding arguments, is that, for any particular type of complex, as one increases the atomic number of the

TABLE III
INTENSITY DATA FOR $\text{Fe}(\text{CO})_4\text{X}_2$, $[\text{Mn}(\text{CO})_4\text{X}_2]^-$, $[\text{Mn}(\text{CO})_4\text{XY}]^-$,
AND $\text{Mn}_2(\text{CO})_8\text{X}_2$ COMPLEXES

Compound	Solvent ^a	$A \times 10^{-2}$ (liter mole ⁻¹ cm ⁻²) ^b				Specific intensity	References
<i>cis</i> - $\text{Fe}(\text{CO})_4\text{Cl}_2$	a	58	226	142	231	166	109
<i>cis</i> - $\text{Fe}(\text{CO})_4\text{Br}_2$	b	65	285	195	190	184	109
<i>cis</i> - $\text{Fe}(\text{CO})_4\text{I}_2$	b	109	658		153	230	109
	c	140	607		258	251	2
<i>cis</i> - $[\text{Mn}(\text{CO})_4\text{Br}_2]^-$	c	56	537	225	370	347	2
<i>cis</i> - $[\text{Mn}(\text{CO})_4\text{I}_2]^-$	c	121	652	350	471	399	2
<i>cis</i> - $[\text{Mn}(\text{CO})_4\text{BrCl}]^-$	c	33	445	196	463	277	2
<i>cis</i> - $[\text{Mn}(\text{CO})_4\text{BrI}]^-$	c	92	582	193	480	348	2
$\text{Mn}_2(\text{CO})_8\text{Cl}_2$	c	33	802	370	802	251	2
$\text{Mn}_2(\text{CO})_8\text{Br}_2$	c	128	286	442	764	270	2
$\text{Mn}_2(\text{CO})_8\text{I}_2$	c	280	1060	550	939	354	2

^a a, Tetrachloroethylene; b, *n*-hexane; c, chloroform.

^b Bands listed in order of decreasing cm⁻¹. See original papers for assignments (2, 109).

transition metal atom the carbonyl intensities increase. Again the specific intensities of the hexacarbonyls of chromium, molybdenum and tungsten, which are, respectively, 461, 539, and 554×10^{-2} liter mole⁻¹ cm⁻² in *n*-hexane, exhibit the general trend. Some appreciation of the generality of this phenomenon can be obtained by comparing the specific intensities of the following pairs of complexes: $\text{Mn}(\text{CO})_6^+$, $\text{Re}(\text{CO})_6^+$ (Table I); $\text{C}_5\text{H}_5\text{M}(\text{CO})_3$ [M = Mn, Re] (Table III); $\text{M}_2(\text{CO})_{10}$ [M = Mn, Re] (Table VII); $\text{HM}_2(\text{CO})_{10}^-$ [M = Cr, W] (Table VII); and $\text{M}(\text{CO})_5\text{X}$ [M = Mn, Re] and $\text{M}(\text{CO})_5\text{X}^-$ [M = Cr, W] (Table II). However, it appears that the compounds with X = I are exceptional in their behavior.

If there is a halogen atom bonded directly to the transition metal atom a relatively low specific intensity for the molecule results (2, 30, 52, 109). The explanation is probably that the halogen atom increases the effective nuclear charge of the central atom and lowers the energy of the d_π orbitals. This removes some electron density from the p_π orbitals of the carbonyl groups and thus decreases the specific intensity. The effect has even been claimed to be additive for some types of derivatives (109). It has been established that the specific intensity is related to the inductive character of the halogen atom and decreases in the order I > Br > Cl. In some cases, a linear relationship appears to exist (52). Extending these ideas, Nesmeyanov *et al.* (107)

TABLE IV
 ABSOLUTE INTEGRATED INTENSITIES OF ARENE-METAL CARBONYL COMPLEXES

Compound	Solvent ^a	$A \times 10^{-2}$ (liter mole ⁻¹ cm ⁻²)		Specific intensity	Refer- ences
RC ₆ H ₄ COOCH ₃ Cr(CO) ₃					
R = m-COOCH ₃	a	720 (<i>A</i> ₁)	1100 (<i>E</i>)	607	94
<i>p</i> -COOCH ₃	a	550	870	473	94
<i>o</i> -Cl	a	630	910	513	94
<i>m</i> -Cl	a	500	860	453	94
<i>p</i> -Cl	a	490	780	423	94
H	a	580	930	503	94
<i>o</i> -CH ₃	a	590	930	507	94
<i>m</i> -CH ₃	a	610	980	530	94
<i>p</i> -CH ₃	a	650	1070	573	94
<i>o</i> -OCH ₃	a	610	1070	560	94
<i>p</i> -OCH ₃	a	570	990	520	94
C ₆ H ₆ Cr(CO) ₃	b	482	869	450	61
(C ₂ H ₅) ₆ C ₆ Cr(CO) ₃	b	595	999	531	61
(CH ₃) ₃ C ₆ H ₃ Mo(CO) ₃	b	530	940	490	16
C ₅ H ₅ Mn(CO) ₃	b	317	886	401	61
	a	—	—	485	107
C ₃ H ₇ C ₅ H ₄ Mn(CO) ₃	a	—	—	486	107
C ₆ H ₅ CH ₂ C ₅ H ₄ Mn(CO) ₃	a	—	—	483	107
COCH ₂ C ₅ H ₄ Mn(CO) ₃	a	—	—	450	107
C ₆ H ₅ COC ₅ H ₄ Mn(CO) ₃	a	—	—	459	107
CF ₃ COC ₅ H ₄ Mn(CO) ₃	a	—	—	414	107
(C ₂ H ₅) ₂ C ₅ H ₃ Mn(CO) ₃	a	—	—	505	107
C(CH ₃) ₃ (C ₆ H ₅ CO)C ₅ H ₃ Mn(CO) ₃	a	—	—	475	107
(C ₂ H ₅) ₂ (CH ₃ CO)C ₅ H ₂ Mn(CO) ₃	a	—	—	482	107
(C ₂ H ₅) ₃ (CH ₃ CO)C ₅ HMn(CO) ₃	a	—	—	494	107
(C ₂ H ₅) ₄ (CH ₃ CO)C ₅ Mn(CO) ₃	a	—	—	497	107
(C ₂ H ₅) ₄ C ₅ HMn(CO) ₃	a	—	—	530	107
C ₅ H ₅ Re(CO) ₃	a	—	—	536	107
CH ₃ COC ₅ H ₄ Re(CO) ₃	a	—	—	492	107
C ₆ H ₅ COC ₅ H ₄ Re(CO) ₃	a	—	—	514	107
C ₅ H ₅ V(CO) ₄	b	218	747	241	61
C ₅ H ₅ Co(CO) ₂	b	9.6 (<i>A</i> ₁)	11.3 (<i>B</i> ₁)	10.5	61
	c	10.2	12.8	11.5	52
C ₅ H ₅ Fe(CO) ₂ Cl	c	13.1	15.9	14.5	52
C ₅ H ₅ Fe(CO) ₂ Br	c	13.6	16.8	15.2	52
C ₅ H ₅ Fe(CO) ₂ I	c	15.7	17.4	16.6	52
C ₅ H ₅ Fe(CO) ₂ SiCl ₃	d	15.0	19.1	17.1	52
C ₅ H ₅ Fe(CO) ₂ GeCl ₃	d	14.6	17.2	15.9	52
C ₅ H ₅ Fe(CO) ₂ SnCl ₃	d	15.6	17.1	16.4	52
C ₅ H ₅ Fe(CO) ₂ Sn(C ₆ H ₅) ₃	d	15.6	17.5	16.6	52
C ₅ H ₅ Fe(CO) ₂ Sn(CH ₃) ₃	d	16.5	19.4	18.0	52

^a a, Carbon tetrachloride; b, cyclohexane; c, *n*-hexane; d, chloroform.

TABLE V
ABSOLUTE INTEGRATED INTENSITIES OF SOME IRON AND NICKEL COMPOUNDS

Compound	Solvent*	$A \times 10^{-2}$ (liter mole ⁻¹ cm ⁻²)			Specific intensity	References
Fe(CO) ₄ P(C ₂ H ₅) ₃	a	180 (<i>A</i> ₁)	190 (<i>A</i> ₁)	1170 (<i>E</i>)	385	19
Fe(CO) ₄ P(OCH ₃) ₃	a	140	220	1190	390	19
Fe(CO) ₄ CH ₂ =CHCH=CH ₂	b	122	1377		375	109
[Fe(CO) ₄] ₂ CH ₂ =CHCH=CH ₂	b	395	1625	988	376	109
<i>trans</i> -Fe(CO) ₃ [P(C ₂ H ₅) ₃] ₂	a	1290 (<i>E'</i>)			430	19
<i>trans</i> -Fe(CO) ₃ [P(OCH ₃) ₃] ₂	a	1290			430	19
<i>cis</i> -Fe(CO) ₃ C ₆ H ₈	b	342 (<i>A</i> ₁)	885 (<i>E</i>)		409	109
<i>cis</i> -Fe(CO) ₃ CH ₂ =CHCH=CH ₂	a	262	518	351	377	109
	b	258	854		371	109
<i>cis</i> -Fe(CO) ₃ CH ₂ =CCH=CH ₂	b	325	497	398	407	109
$\begin{array}{c} \\ \text{CH}_3 \end{array}$						
<i>cis</i> -Fe(CO) ₃ Cl·H ₂ C=CH—CH ₂	a	238	313	298	283	109
<i>cis</i> -Fe(CO) ₃ Cl·H ₂ C=CH—CHCH ₃	a	260	304	307	290	109
<i>cis</i> -Fe(CO) ₃ Br·H ₂ C=CH—CH ₂	a	254	320	275	283	109
	b	253	310	280	281	109
<i>cis</i> -Fe(CO) ₃ Br·H ₂ C=CH—CH—CH ₃	a	243	323	273	280	109
<i>cis</i> -Fe(CO) ₃ Br·H ₂ C=CHCHCO ₂ CH ₃	a	247	269	234	250	109
<i>cis</i> -Fe(CO) ₂ [P(OCH ₃) ₃] ₃	a	170 (<i>A</i> ₁)	590 (<i>B</i> ₁)		380	19
Ni(CO) ₃ P(C ₂ H ₅) ₃	a	100 (<i>A</i> ₁)	800 (<i>E</i>)		300	19
Ni(CO) ₃ P(OCH ₃) ₃	a	80	720		270	19
Ni(CO) ₂ [P(C ₂ H ₅) ₃] ₂	a	210 (<i>A</i> ₁)	470 (<i>B</i> ₁)		340	19
Ni(CO) ₂ [P(OCH ₃) ₃] ₂	a	200	460		330	19
Ni(CO)[P(OCH ₃) ₃] ₃	a	310			310	19

* a, *n*-Hexane; b, tetrachloroethylene.

TABLE VI
ABSOLUTE INTEGRATED INTENSITIES OF SOME MOLYBDENUM COMPOUNDS

Compound	Solvent ^a	$A \times 10^{-2}$ (liter mole ⁻¹ cm ⁻²)				Specific intensity	References
<i>trans</i> -Mo(CO) ₄ [P(OCH ₃) ₃] ₂	a		2197 (<i>E_a</i>)			549	53
	b	50 (<i>B_{1g}</i>)	1980			495	16
<i>trans</i> -Mo(CO) ₄ [P(OC ₆ H ₅) ₃] ₂	a		1911			478	53
<i>trans</i> -Mo(CO) ₄ [P(C ₂ H ₅) ₃] ₂	b		2010			500	16
<i>cis</i> -Mo(CO) ₄ [P(C ₂ H ₅) ₃] ₂	b	145 (<i>A₁</i>)	330 (<i>A₁</i>)	840 (<i>B₂</i>)	490 (<i>B₁</i>)	450	16
<i>cis</i> -Mo(CO) ₄ [Sb(C ₂ H ₅) ₃] ₂	b	200	360	850	520	480	16
<i>cis</i> -Mo(CO) ₃ [P(C ₂ H ₅) ₃] ₃	b		540 (<i>A₁</i>)		1130 (<i>E</i>)	560	16
<i>cis</i> -Mo(CO) ₃ [P(CH ₃) ₃] ₃	b		550		1070	530	16
<i>cis</i> -Mo(CO) ₃ [P(OCH ₃) ₃] ₃	b		540		1160	570	16
	a		608		1251	620	53
<i>cis</i> -Mo(CO) ₃ [PCl ₂ (OCH ₃)] ₃	b		520		830	450	16
<i>cis</i> -Mo(CO) ₃ [PCl ₃] ₃	b		500		750	420	16

^a a, *n*-Hexane; b, cyclohexane.

TABLE VII
ABSOLUTE INTEGRATED INTENSITIES OF POLYNUCLEAR METAL CARBONYL
COMPOUNDS

Compound	Solvent ^a	$A \times 10^{-2}$ (liter mole ⁻¹ cm ⁻²)			Specific intensity	Refer- ences
[C ₅ H ₅ Fe(CO) ₂] ₂	a	234	475	549 ^b	355	275 ^b 109
	b	790	582 ^b		395	291 ^b 108
Co ₂ (CO) ₈	c	2325	282 ^b		388	141 ^b 109
	b	2320	323 ^b		387	162 ^b 109
	b	1715	269 ^b		286	135 ^b 108
Mn ₂ (CO) ₁₀	c	643 (B ₂)	1650 (E ₁)	430 (B ₂)	272	136
	d	617	1850	406	287	136
	e	647	2349	534	353	136
	f	660	2614	573	385	136
	b	3361			336	108
Re ₂ (CO) ₁₀	d	456	2349	769	357	136
	b	3630			363	108
ReMn(CO) ₁₀	b	3439			344	108
HCr ₂ (CO) ₁₀ ⁻	f	94	3565	1294	495	136
HW ₂ (CO) ₁₀ ⁻	f	155	4516	1654	633	136
[C ₅ H ₅ Mo(CO) ₃] ₂	b	2631			439	108
C ₅ H ₅ FeRe(CO) ₇	b	2645			378	108
C ₅ H ₅ MoRe(CO) ₈	b	3265			408	108
C ₅ H ₅ WRe(CO) ₈	b	3317			415	108
C ₅ H ₅ MoMn(CO) ₈	b	2940			368	108
C ₅ H ₅ WMn(CO) ₈	b	2992			374	108
Fe ₃ (CO) ₁₂	a	3544	200 ^b		296	— ^b 109
	c	3610	— ^b		300	— ^b 109
Co ₄ (CO) ₁₂	c	2700	703 ^b		300	234 ^b 109

^a a, Tetrachloroethylene; b, carbon tetrachloride; c, *n*-hexane; d, cyclohexane; e, chloroform; f, tetrahydrofuran.

^b Bridging carbonyl groups.

demonstrated that, for a series of cyclopentadienyl tricarbonyl manganese and rhenium derivatives, the specific intensities decrease with the electron acceptor ability of the ring substituents. In other words, the electronic effects are transmitted from the cyclopentadienyl ring via the central metal atom onto the carbonyl groups. In contrast, the specific intensities of a series of substituted benzoic methyl ester tricarbonyl chromium derivatives were found to give small variations which could not be correlated with the properties of the substituents (94).

TABLE VIII^a
CONVERSION FACTORS OF INTENSITY UNITS TO PRACTICAL UNITS

Unit	Dimensions	Multiplicative factor which converts into practical units	Comments
IUPAC Practical	$\text{cm}^{-2} \text{ mole}^{-1}$ liter	1	The unit A or A_{RJ} used by Ramsay and Jones has the same dimensions but requires an additional conversion factor of 0.4343. Mecke introduced a unit which has been denoted by both A and A_M ($\text{cm}^3 \text{ mole}^{-1}$) which is related to A_{RJ} by the approximate relationship $A_M = 10^{-3} \nu_0^2 A_{RJ}$ where ν_0 is the band maximum in cm^{-1} . The unit of "darks" (cm mmole^{-1}) is numerically identical to A_{RJ} .
IUPAC Absolute	$\text{cm}^2 \text{ sec}^{-1}$ molecule^{-1}	8.728×10^9	Identical to the unit introduced by Thompson (131a) but which has been denoted by both B and A_T .
IUPAC Secondary	$\text{cm}^2 \text{ molecule}^{-1}$	approx. $2.617 \times 10^{20} \nu_0$, where ν_0 is the band maximum in cm^{-1}	Crawford introduced the unit A_C (or Q or I) but did not unambiguously define the dimensions which may be either $\text{cm}^2 \text{ mole}^{-1}$ (0.1660×10^{-23}) or $\text{cm}^2 \text{ mmole}^{-1}$ (0.1660×10^{-20}), conversion factors to the secondary unit being given in brackets. Seshadri and Jones (125), however, have chosen to equate A_C with the secondary unit.

^a More extensive tables are given in (65a) and (125).

Finally, a rather novel use has been made of the specific intensities of metal carbonyl stretching vibrations. By determining the specific intensities of homonuclear dimetal carbonyl complexes and transferring them to

corresponding heteronuclear dimetal derivatives, Nesmeyanov *et al.* (108) were able to predict the specific intensities of the modes of the latter and assess the probable molecular geometry of the heteronuclear species. In this study it was also pointed out, in agreement with earlier work (109), that bridging carbonyls have lower specific intensities than terminal carbonyls, though the explanation of this phenomenon must await a more detailed study.

XI

CONCLUSION

Although it is somewhat surprising that almost any method of analyzing relative or absolute intensity data leads to physically reasonable values for bond angles, this application of intensity measurements has proved to be of value in carbonyl chemistry and its use is likely to continue. When a molecule contains carbonyl groups which are not symmetry-related it has proved more difficult to calculate reliable bond angles, but it seems certain that as vibrational analyses of such molecules are refined a deeper understanding of the corresponding band intensities will follow. Conversely, intensity data provide a useful additional criterion by means of which force constant analyses may be judged. In this connection it may be remarked that the simple CKM force field and its modifications have been surprisingly successful.

In this chapter we include the first compilation of reported absolute intensity data for metal carbonyl species. We have attempted to refer this data to a common set of units but the literature contains ambiguities which it has not always proved possible to resolve. Absolute intensity data such as these provide an indication of the extent to which the vibrations of a metal carbonyl derivative are affected by the solvent in which they are studied. Present indications are that solvent-solute interactions are of prime importance and it would be most useful to have gas-phase absolute intensity data with which to compare solution measurements.

For both absolute and relative intensity measurements the question of the accuracy of Ramsay's method of analyzing the experimental data remains. A superior technique has been suggested. Cabana and Sandorfy have described an extension of Ramsay's method involving the measurement of peak heights at seven or more different positions, thereby reducing the dependence of the results on an assumed form for the band profile (125).

The general conclusion seems clear. The intensity measurements that have been made to date are susceptible to significant errors or distortions from a variety of effects. However, they appear to be quite unambiguous in their consistency with the current ideas of bonding in carbonyl species and suggest that this is an area of chemistry which it would be worth while to explore in greater depth.

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Organometallic Aspects of Diboron Chemistry*

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I. Introduction	237
II. Some General Features of Diboron Chemistry	238
A. Preparation of Diboron Compounds	238
B. Structural and Thermochemical Properties of Diboron Compounds	247
C. Thermal Stability of Diboron Compounds	249
III. Reactions of Diboron Tetrahalides with Unsaturated Compounds	251
A. Addition to Olefins and Acetylenes	251
B. Stereochemistry of the Addition Reaction	254
C. Reactions with Haloolefins	257
D. Reactions with Aromatic Hydrocarbons	260
E. Reactions with Unsaturated Organometallic Derivatives	261
F. Reactions with Other Unsaturated Molecules	263
IV. Properties of Some Diboration Products	265
References	269

I

INTRODUCTION

Formally subvalent compounds of boron containing a boron-boron single bond are intermediate in structural complexity between simple monoboron derivatives and the polyhedral electron-deficient compounds of the element. The properties of such compounds, particularly the simple derivatives of the B_2X_4 type, have attracted the attention of several groups of workers since Stock's initial discovery of B_2Cl_4 some 45 years ago (96). These materials provide the simplest examples of catenation in boron chemistry and offer suitable systems in which to study the properties of the covalent B—B bond and the characteristic chemistry of compounds containing this linkage.

Studies of the general chemistry of compounds containing the B—B linkage have been reviewed (13, 56). The boron subhalides have also been discussed at some length in general reviews of boron halide chemistry (67, 101).

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For the organometallic chemist, two aspects of the chemistry of this class of compounds are particularly relevant. There is, first, a somewhat limited chemistry of derivatives containing boron-carbon bonds in which the boron-boron bond is also present. Synthesis and properties of such organodiboron derivatives, and, indeed, even authentic synthetic failures in this area, are of interest in comparison with the rich organic chemistry of monoboron derivatives. Second, the chemistry of subvalent boron compounds and their interactions with organic and organometallic systems can lead to novel reactions and to organoboron derivatives accessible with difficulty, if at all, from more conventional precursors.

This chapter will concentrate primarily on features of the chemistry of diboron compounds of particular interest from the organometallic viewpoint. While our limited scope does not permit a comprehensive review of all aspects of diboron chemistry, we will initially survey some general features of the subject, with emphasis on unique synthetic aspects and on properties particularly characteristic of compounds containing a simple electron-pair bond between boron atoms. Electron-deficient polyboron compounds will be specifically excluded from consideration. More extensive consideration will be given to the interaction of diboron compounds with unsaturated organic systems, which is a major aspect of organometallic chemistry based on boron-boron-bonded systems. Finally, we shall survey some of the chemistry of particular organoboron compounds derived from diboron precursors.

II

SOME GENERAL FEATURES OF DIBORON CHEMISTRY

A. Preparation of Diboron Compounds

Synthesis of specific diboron compounds may involve either (1) reductive coupling reactions of monoboron derivatives to form materials containing the boron-boron bond, or (2) reactions of compounds possessing preformed B_2 fragments. Since the formation of the boron-boron bond is in a sense the central synthetic difficulty in diboron chemistry, it is of interest to consider in some detail the approaches of various workers to this problem.

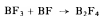
1. Preparations Involving Formation of B—B Bonds

The earliest synthesis of a characterized diboron species was the preparation of B_2Cl_4 by Stock (96), using an electric discharge between zinc electrodes immersed in liquid BCl_3 . A number of discharge procedures have since been reported for the synthesis of B_2Cl_4 (40, 52, 70, 104, 109, 110). Spectroscopic evidence from microwave excitation (60) and flash photolysis (71) experiments suggests that the mechanism involves formation of the carbenelike species, BCl , which inserts into the boron–chlorine bond of a BCl_3 molecule to form the subhalide. Urry (101) has suggested, however, that a different mechanism may prevail in the synthesis in a mercury arc.

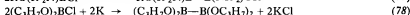
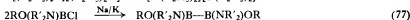
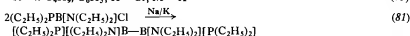
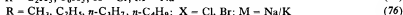
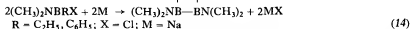
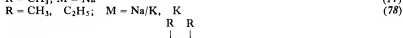
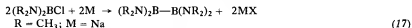
A well-documented procedure (110) involving a high-voltage discharge in BCl_3 vapor between copper wool electrodes is particularly satisfactory for preparation of B_2Cl_4 in laboratory quantities. Formation of B_2Br_4 and B_2I_4 from the trihalides by discharge methods has also been reported (33, 94). Early attempts to prepare B_2F_4 from BF_3 in a discharge between mercury electrodes were unsuccessful (38). The subfluoride has been obtained, however, in the products of a microwave discharge in BF_3 using an alumina reactor. In a silica discharge tube, formation of oxyfluoride species predominates, apparently because of the attack of reactive fluorine-containing species on the walls of the reactor (12).

Conventional chemical reduction of boron trihalides with active metals, metal borides, hydrogen plus metal, or other reducing agents is not a satisfactory route to the diboron tetrahalides (13, 104), although this approach is useful for the preparation of other diboron derivatives (*vide infra*). A novel synthesis of B_2Cl_4 has been reported by Timms, who condensed BCl_3 at $-196^\circ C$ with copper atoms produced by vaporization of the metal (99). On warmup, reaction occurred with formation of B_2Cl_4 in good yield. A similar reaction with dichloromethylborane gave 1,2-dichloro-1,2-dimethyldiborane(4), the first reported example of a methylhalo diboron derivative.

Timms has also reported another high-temperature approach to the formation of B—B bonds by the insertion of BF (formed at $2000^\circ C$ from boron and BF_3) into the B—F bond (98):

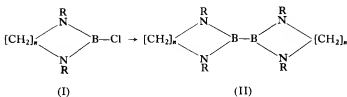


Although active-metal reduction of boron trihalides to B_2X_4 compounds has in general been unsuccessful, formation of boron-boron bonds by the reaction of chloroboranes with alkali metals provides a useful route to a number of diboron derivatives. It is of interest to note that what may be considered the prototype of this reaction was reported by Stock and Pohland (97), who prepared tetraborane(10) from iododiborane(6) and sodium. Formation of tetramethoxy- and tetraethoxydiborane(4) from the corresponding dialkoxychloroboranes and sodium was reported by Wiberg and Ruschmann (114), although later workers were unable to reproduce the synthesis of the ethoxy derivative (16). More recently, however, the procedure has been successfully applied to the synthesis of a number of diboron derivatives in reactions such as the following:



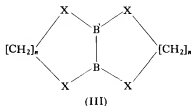
The coupling procedure appears to be well suited to the formation of dialkylamino- and mixed alkyl-dialkylaminodiboron derivatives. It is less satisfactory for the formation of diboron esters of low molecular weight alcohols.

The coupling reaction has also been applied to cyclic derivatives of type (I). Products in each case were identical to those prepared from tetrakis-(dimethylamino)diborane(4) by transamination with the appropriate diamine and were formulated as having structures of type (II) (20). Mass spectrometric fragmentation patterns suggest, however, that $B_2[(CH_3N)_2(CH_2)_2]$ and analogous heterocyclic compounds derived from ethylene glycol and ethanedithiol may have the fused ring structure (III), implying a structural rearrangement in the coupling reaction of the amine derivative (21).



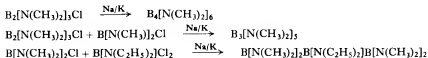
$n = 2$; $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{iso-C}_3\text{H}_7$

$n = 3$; $\text{R} = \text{CH}_3$

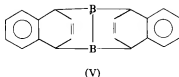
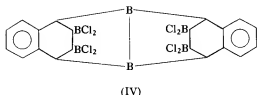


$n = 2$; $\text{X} = \text{CH}_3\text{N}, \text{O}, \text{S}$

Formation of more extended boron chains by the coupling reaction has been reported (48):



Attempts to prepare tetraalkyldiborane(4) derivatives from dialkylhaloboranes have been unsuccessful, owing apparently to the inherent thermal instability of these organodiboron compounds, which leads to rapid formation of trialkylborane and other products (77, 113). A material of empirical formula $(n\text{-C}_4\text{H}_9)_2\text{B}$ has been reported from the reaction of $(n\text{-C}_4\text{H}_9)_2\text{BCl}$ with sodium-potassium alloy. This substance, of unknown complexity, was unstable and disproportionated to $(n\text{-C}_4\text{H}_9)_3\text{B}$ and a solid presumed to be $n\text{-C}_4\text{H}_9\text{B}$ (6). Possible formation of sodium salts of tetraphenyldiborane(4) from the reaction of sodium with chlorodiphenylborane has been noted (13). Reaction of sodium naphthalenide with B_2Cl_4 at room temperature was reported to yield a liquid product of composition $(\text{C}_{10}\text{H}_8)_2\text{B}_2(\text{BCl}_2)_4$, for which structure (IV) was suggested. The compound adds 4 moles of $(\text{CH}_3)_3\text{N}$ to form an adduct which decomposes above 100°C to yield the



bis(trimethylamine) adduct of B_2Cl_4 and an unstable product thought to be (V) (63).

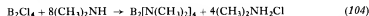
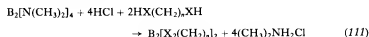
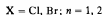
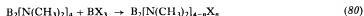
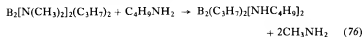
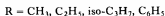
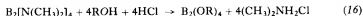
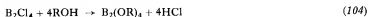
It is reported that the trimethylamine complex of tetramethyldiborane(4) was obtained from the reduction of bromodimethylborane with sodium or silver in trimethylamine (92).

A compound formulated as tetraallyldiborane(4) was obtained, along with diallyl, by thermal disproportionation of triallylborane. The formulation was supported by boron analyses and molecular weight (116). An alternative structure, not involving a boron-boron bond, has been suggested as more probable, however (13).

The presence of boron-boron bonds has been suggested in dimeric complexes formed by reaction of some triarylboron compounds with active metals in ethereal solution (25, 73) although alternative structures have been proposed (44). The salt $Na_2[(CH_3)_2BH]$, formed from tetramethyldiborane(6) and sodium in liquid ammonia, reacts with trimethylborane in that solvent to form $Na_2[B_2H(CH_3)_5]$, which also may contain a boron-boron bond (22).

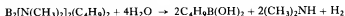
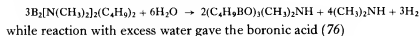
2. Preparations Involving Preformed B—B Bonds

A fairly extensive metathetical chemistry of diboron compounds has been developed which provides the means for synthesis of specific derivatives from more commonly available starting materials such as tetrachlorodiborane(4) and the tetrakis(dialkylamino)diboron derivatives. Thus, reactions involving hydrolysis, aminolysis, alcoholysis, transamination, etc., are available for interconversions of diboron compounds by pathways analogous to those known in monoboron chemistry. Examples of such reactions include the following:

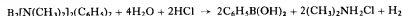


It is of interest that the B—N bonds in $\text{B}_2[\text{N}(n\text{-C}_4\text{H}_9)_2]_4$ and $\text{B}_2[\text{N}(\text{CH}_3)_2]_4$ appear to be significantly more stable to hydrolysis in acetone-water or tetrahydrofuran-water solutions than those in the corresponding triaminoboranes, although $\text{B}_2[\text{NH}(\text{CH}_3)]_4$ hydrolyzes rapidly. It has been suggested that greater steric hindrance in the dialkylaminodiboron compounds may restrict the approach of water molecules or formation of a tetrahedral transition state (15).

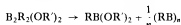
Reactions of this type are somewhat less satisfactory for preparation of mixed diboron derivatives containing boron-carbon bonds. Thus, while tetrakis(dimethylamino)diborane(4) is readily hydrolyzed to tetrahydroxydiborane(4) in aqueous acid, 1,2-bis(dimethylamino)-1,2-diethylborane(4) reacts with formation of hydrogen and cleavage of the boron-boron bond (14). Reaction of the dibutyl analog with a twofold excess of water gave the dimethylamine adduct of the boroxole



The diphenyl derivative was recovered unchanged from aqueous hydrochloric acid, but cleavage occurred under homogeneous conditions in tetrahydrofuran (14).

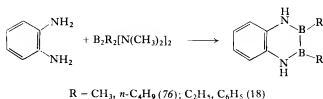
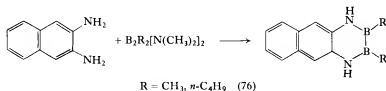


Similarly, attempted methanolysis of $B_2[N(CH_3)_2]_2(C_2H_5)_2$ resulted in boron-boron bond cleavage (14), as did the reaction of the dibutyl analog with excess butanol (76). Products apparently arising from disproportionation of unstable dialkyldialkoxydiboron derivatives

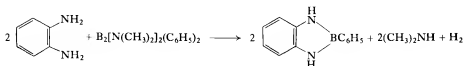


were obtained from reactions of $B_2[N(CH_3)_2]_2(C_4H_9)_2$ with butanol in 1:2 ratio and from the low-temperature ($-70^\circ C$) reaction of $B_2[N(CH_3)_2]_2(C_3H_7)_2$ with stoichiometric amounts of methanol and hydrogen chloride. Reaction of butyl mercaptan with $B_2[N(CH_3)_2]_2C_4(H_9)_2$ also gave disproportionation products.

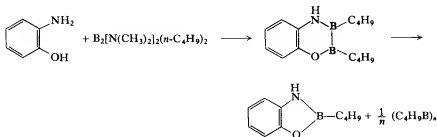
Transamination of $B_2[N(CH_3)_2]_2(C_3H_7)_2$ with butylamine, however, gave the anticipated product, $B_2[NHC_4H_9]_2(C_3H_7)_2$ (76). A number of heterocyclic organodiboron derivatives have been obtained by transamination of dialkylbis(dialkylamino)diborane(4) derivatives with *o*-diamines, e.g.,



In the latter reaction, with bis(dimethylamino)diphenyldiborane(4), some cleavage of the boron-boron bond was observed. The proposed reaction is

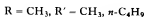
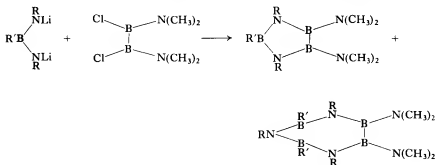


Reaction of $B_2[N(CH_3)_2]_2(n-C_4H_9)_2$ with *o*-aminophenol gave an unstable heterocycle which underwent subsequent disproportionation

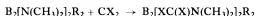


as did the corresponding derivative obtained from reaction of the diboron compound with catechol (76).

Organoboron heterocycles containing the boron-boron bond have also been prepared by the reaction of *N*-lithio derivatives of alkylbis(alkylamino)-boranes with 1,2-dichloro-1,2-bis(dimethylamino)diborane(4) (74):



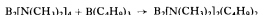
Diorganobis(dimethylamino)diborane(4) derivatives react with carbon dioxide or carbon disulfide in petroleum ether to form the products of insertion into the boron-nitrogen bond (1):



Reaction of 1,2-bis(dimethylamino)-1,2-diethyldiborane(4) with boron trifluoride gave ethyldifluoroborane, dimethylaminodifluoroborane, and a residue whose composition (by difference) was $(C_2H_5B)_n$. A reaction

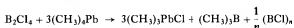
sequence was suggested involving initial interchange of fluoro and dimethylamino groups, followed by disproportionation of an unstable intermediate, diethyldifluorodiborane(4) (14).

There are relatively few examples of formation of boron-carbon bonds in compounds containing preformed boron-boron fragments. The preparation of dibutylbis(dimethylamino)diborane(4) by alkyl-amino exchange has been noted (77).



The compound prepared in this way is the symmetric isomer obtainable also by the active metal coupling reaction or by the reaction of butyllithium with the product obtained from treatment of $\text{B}_2[\text{N}(\text{CH}_3)_2]_2(\text{C}_4\text{H}_9)_2$ with HCl (79). Formation of a compound formulated as 9,10-dibora-9,10-bis(dimethylamino)phenanthrene has been reported from the reaction of 1,2-bis(dimethylamino)-1,2-dichlorodiborane(4) with magnesium and 2,2'-dibromobiphenyl (83).

Efforts to alkylate diboron tetrahalides with organometallic reagents have been comparatively unsuccessful until quite recently. Reactions of B_2Cl_4 with dimethylzinc were reported to yield only trimethylborane and unidentified black solids presumed to contain elemental boron. It was suggested that methylated diboron derivatives, once formed, were unstable with respect to irreversible decomposition or that the organometallic reagents used were functioning as reducing agents (104). Tetramethyllead, which converts BCl_3 quantitatively to trimethylborane, gave the same compound as the only volatile product when treated with a deficiency of B_2Cl_4 (49). The reaction was formulated as



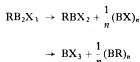
and was presumed to involve disproportionation of partially methylated B_2Cl_4 .

Holliday and Taylor (59) have studied the reactions of tetrafluorodiborane(4) with several organometallic reagents. No evidence was obtained for the formation of organo-substituted diboron compounds. Reaction with diphenylmercury led to reduction of a major fraction of the organometallic to metallic mercury, with formation of difluorophenylborane and BF_3 . Diethylmercury was reduced similarly, with formation of ethyldifluoroborane, BF_3 , and ethane. With tetravinyltin, the major products

were ethylene and difluorovinylborane. More recently, preparation of trichloromethyldiborane(4) from the reaction of B_2Cl_4 with dimethylmercury has been reported. Explosion hazards have been noted in this preparation (41).

In a study of the reactions of B_2Cl_4 and B_2F_4 with the Group IV tetramethyl derivatives, Ritter (84) obtained evidence for methylation of the chloride by tetramethylgermanium, -tin, and -lead to form $CH_3B_2Cl_3$. Yields of the methyldiboron compound were dependent upon reaction conditions and handling. Completely quantitative separation of the compound could not be effected, although $B_2Cl_4/CH_3B_2Cl_3$ fractions containing up to 90% of the methyl derivative were obtained. Characterization was based on demonstration of the ions $CH_3B_2Cl_2^+$ and $CH_3B_2Cl_3^+$ in the mass spectrum, molecular weight, formation of hydrogen on alkaline hydrolysis, formation of methane on protonolysis and ammoniacal silver cleavage, chloride analyses, and infrared spectra.

Evidence for oxidation-reduction processes was also obtained in the case of reactions with tetramethyltin and -lead. Solid products containing Sn(II) were detected by Mössbauer spectroscopy in the tetramethyltin system, and, indeed, the gas-phase reaction of this reagent and tetrafluorodiborane(4) at room temperature gives a rapid formation of a metallic mirror in the reaction vessel. Moreover, with the heavier Group IV alkyls, the total yield of volatile boron-containing species amounted to significantly more than half the total amount of boron originally taken as subhalide. An alkylation-disproportionation sequence would be expected to yield half the boron originally present as boron (II) in the form of boron(III) derivatives, assuming that the alkylidiboron compound decomposes in a manner analogous to B_2Cl_4 :



Oxidation by the quadrivalent metal, however, would be expected to result in formation of greater quantities of trivalent boron compounds, as observed.

B. Structural and Thermochemical Properties of Diboron Compounds

Little or no detailed physical information is available concerning diboron compounds with organic groups bonded to boron. Most of the available

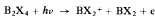
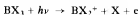
structural data refer to the diboron tetrahalides. X-Ray diffraction studies of B_2Cl_4 (5) and B_2F_4 (100) indicate a planar, centrosymmetric structure (D_{2h}) in the solid. Electron diffraction (47) and infrared and Raman studies (65) suggest that the B_2Cl_4 molecule has a skewed (D_{2d}) structure in the gas and liquid. The infrared spectrum of B_2F_4 (37, 42) indicates it to be skewed or undergoing essentially free rotation in the gaseous state.

The B—Cl distance in solid B_2Cl_4 (1.728 ± 0.020 Å) is only slightly shorter than that in BCl_3 (1.75 Å), while the B—F bond in solid B_2F_4 (1.32 ± 0.04 Å) is similar to, or perhaps slightly longer than, the bond length in BF_3 (spectroscopic value: 1.29 Å). The B—B bond distance in the chloride (1.75 ± 0.05 Å) does appear, however, to be significantly longer than that in the fluoride (1.67 ± 0.04 Å).

Infrared and Raman studies suggest that the $B_2O_4C_4$ skeleton of the $B_2(OCH_3)_4$ molecule is planar. In the same study, it was concluded that the two BN_2 planes of $B_2(NMe_3)_4$ are skewed at about 30° to one another (8).

Thermochemical data for diboron compounds are rather limited. The heats of chlorination of B_2F_4 (45) and B_2Cl_4 (46) have been utilized to derive heats of formation of these halides. From these, with the additional assumption that the average thermochemical bond energies $E(B-X)$ are identical in BX_3 and B_2X_4 , boron-boron bond energies of 72.4 and 79 kcal/mole were obtained for B_2F_4 and B_2Cl_4 , respectively. With a similar assumption regarding the value of $E(B-OH)$, a calorimetric study of the oxidation by aqueous silver ion of $B_2(OH)_4$ led to a value of 84 ± 5 kcal/mole for $E(B-B)$ in the latter compound (36). Approximate constancy of $E(B-B)$ in B_2X_4 compounds (79 ± 5 kcal/mole) was assumed in estimating heats of formation of B_2Br_4 and B_2I_4 (36).

Rather different, and higher, values of the boron-boron bond energies were obtained by Dibeler and his co-workers from photoionization mass spectrometric studies of B_2F_4 and B_2Cl_4 and the corresponding trihalides. Essentially, this work combines known heats of formation of the subhalides (106) with threshold energies for dissociative ionization processes such as



With the usual assumptions as to the absence of excess energy, these studies led to B—B bond dissociation energies, $D(B-B)$, of 103.1 kcal/mole in B_2F_4 (31) and 87.6 kcal/mole in B_2Cl_4 (32).

Availability of Dibeler's values for the energies of the boron-boron bonds allows a test of the assumption, used in the earlier work, that $E(\text{B}-\text{X})$ is unchanged from BX_3 to B_2X_4 . A simple calculation shows the average thermochemical B—F bond energy in B_2F_4 is about 8 kcal/mole lower than in BF_3 . A similar but less pronounced difference (~ 2.5 kcal/mole) is found for the chlorides. These differences may account, at least in part, for the pronounced nonrandom distribution of halogens in systems containing both monoboron and diboron moieties (85).

C. Thermal Stability of Diboron Compounds

Diboron derivatives differ markedly in thermal stability and mode of decomposition. In general there is a pronounced tendency for higher stability to be associated with the presence of unshared electron pairs on the atoms bonded directly to boron. This suggests that stability may be enhanced if the coordinative unsaturation at the boron atom can be reduced by partial $p\pi-p\pi$ double bonding.

As noted previously, no tetraalkyl- or tetraaryldiboron derivatives have been definitively characterized, although their preparation has been attempted. The recovery of trialkylboranes and involatile residues from these reactions suggests that disproportionation reactions occur:



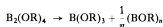
As described above, the bis(trimethylamine) complex of tetramethyldiborane(4) may be rather more stable than the parent compound.

Similarly, the parent hydride, diborane(4), has been prepared only in the form of complexes with Lewis bases (30, 43, 72). Attempted reduction of B_2Cl_4 with various metallic hydrides leads to the formation of diborane(6) and other boron hydrides (104, 109).

At the other extreme, the most stable derivatives of the B_2X_4 type appear to be the tetrakis(dialkylamino) compounds. Thus, tetrakis(dimethylamino)-diborane(4) is stable at its boiling point of 206°C (17). The compound decomposes at 300°C to form bis(dimethylamino)borane and involatile residues containing B—C bonds. It is reported that tetra(*N*-methylanilino)-borane(4) is pyrolyzed at 300°C by a different mechanism to yield *N*-methylaniline (18).

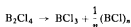
Tetraalkoxydiboron compounds are somewhat less stable than their dialkylamino analogs. The methyl and ethyl derivatives are stable, respec-

tively, to 110° and 90° C (16). At higher temperatures they may disproportionate:



Dialkyl ethers are also found among the decomposition products (13).

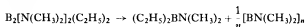
Tetrachlorodiborane(4) decomposes at room temperature or below to yield BCl_3 and colored solid materials. The thermal disproportionation is often represented as



The solid products are, however, more complex than indicated by this equation. Among the materials obtained from the decomposition products are pale yellow B_4Cl_4 (105), B_8Cl_8 (3), a red solid described as $(\text{BCl}_{0.9})_x$ (105) and subsequently formulated as $\text{B}_{12}\text{Cl}_{11}$ (93) or possibly $\text{B}_{11}\text{Cl}_{11}$ (69) a purple paramagnetic subchloride (103), and a white involatile solid that analyzes as $(\text{BCl}_{0.6})_x$ (105). Despite the obvious formation of deep coloration in B_2Cl_4 samples held at room temperature, the compound is sufficiently robust to permit manipulation by conventional vacuum line techniques. Decomposition to the extent of 13% in 29 hours or 33% in 534 hours has been reported for gaseous samples at 25° C and ~90 torr (7), while 90% of the initial B_2Cl_4 was recovered from 33 mole% solutions in hexane or ethyl chloride after 6 days at 25° C (84). A kinetic study of the gas-phase decomposition at 138–155° C suggested that the reaction is second-order, heterogeneous, and strongly retarded by the decomposition products (7). As noted below (Section III,C), decomposition of B_2Cl_4 is markedly inhibited in the presence of some haloolefins.

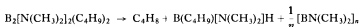
Tetrafluorodiborane(4) is considerably more stable than the chloride. It is reported to decompose very slowly at room temperature, while heating at 200° C for several hours led to decomposition of 40% of the material to BF_3 and a yellow, involatile solid (38).

The presence of dialkylamino groups in mixed alkyl-amino or aryl-amino diboron compounds confer considerable thermal stability. Brotherton and his co-workers found that 1,2-bis(dimethylamino)-1,2-diethyldiborane(4) is stable to about 140° C. At 200° C slow decomposition occurs, probably a disproportionation:



At 300°C, the reaction is more complex and hydrogen, ethane, and traces of dimethylamine appear in the products along with the dimethylamino-diethylborane (14).

Thermal decomposition of 1,2-dibutyl-1,2-bis(dimethylamino)diborane (4) at 200°–230°C was found by Nöth and Fritz to yield 1-butene and butyl-(dimethylamino)borane, the reaction postulated being

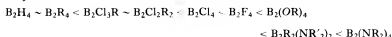


These authors suggested that a similar reaction occurs with the ethyl analog to produce ethylene, which reacts with $\text{B}(\text{C}_2\text{H}_5)[\text{N}(\text{CH}_3)_2]\text{H}$ to form the dimethylaminodiethylborane (76).

As noted above (Section II,A), dialkyldialkoxydiboron compounds appear to be unstable at room temperature.

Methylchlorodiboron compounds are somewhat less stable than B_2Cl_4 . The 1,2-dichloro-1,2-dimethyldiborane (4) prepared by Timms was observed to decompose above -20°C (99). Similarly, Ritter noted decomposition of trichloromethyldiborane (4) in B_2Cl_4 solution at -80°C with the formation of dichloromethylborane and BCl_3 (84).

The results of various workers on the thermal stability of diboron derivatives may be summarized in the following approximate order of stability:

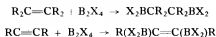


III

REACTIONS OF DIBORON TETRAHALIDES WITH UNSATURATED COMPOUNDS

A. Addition to Olefins and Acetylenes

One of the most interesting and characteristic reactions of the diboron tetrahalides is their ready addition across carbon-carbon double and triple bonds. This process, which has been called "diboration" (101) by analogy to the well-known hydroboration reaction, provides a convenient route to vicinal bis(dihaloboryl)organic derivatives:



The resulting compounds may be converted to other bis(boryl) derivatives by a variety of metathetical reactions appropriate to organoboron dihalides, by oxidative hydrolysis to *vic*-diols, or, in certain cases, to hydrocarbons by protonolysis.

The first example of this reaction was reported by Schlesinger and his co-workers (102), who obtained 1,2-bis(dichloroboryl)ethane in yields approaching 100% from the reaction of B_2Cl_4 with ethylene at $-80^\circ C$. The product is a liquid boiling at $142^\circ C$ and freezing at $-28.5^\circ C$. The vapor is monomeric. The structure has been confirmed by a crystallographic study (4) which showed that the molecule has a planar $Cl_2BCCBCl_2$ skeleton in the solid with a *trans* configuration of the BCl_2 groups.

The addition reaction has been observed with a variety of olefins, acetylenes, and with cyclopropane (23). Both B_2Cl_4 and B_2F_4 can add to suitable unsaturated molecules. Unsuccessful attempts to achieve similar reactions with tetraamino and tetraalkoxydiboron compounds and with 1,2-bis(dimethylamino)-1,2-diethyldiborane(4) have been noted (13, 68). Evidence for formation of bis(boryl) derivatives from the reaction of mixtures of $B_2[N(CH_3)_2]_4$ and BCl_3 with olefins has been mentioned (115); the reaction was presumed to involve a mixed dimethylaminochlorodiboron derivative. Lewis base complexes of B_2Cl_4 are unreactive toward olefins (56).

Most workers have presumed that the addition reaction proceeds via π -donation from the olefin into the vacant p orbitals of the diboron compound (55). Stereochemical evidence (discussed more fully below, Section III,B) is in general agreement with such a four-center mechanism, and there is as yet no convincing evidence for an alternative. The involvement of the boron p orbitals is clearly indicated by the lack of reactivity of B_2Cl_4 -base complexes as well as by the failure to obtain addition with compounds such as the aminodiborons in which the coordinative saturation at the boron atoms can be removed or reduced by $p\pi-p\pi$ bonding.

Data on the relative reactivity of monoolefins towards B_2Cl_4 and B_2F_4 are qualitative or, at best, semiquantitative. A few generalizations can, however, be made:

(1) With a given olefin, B_2Cl_4 reacts significantly more rapidly than B_2F_4 . Under comparable conditions at $35^\circ C$, for example, a 1 : 1 mixture of *tert*-butylethylene and B_2Cl_4 is 50% converted to addition product in 30 minutes, while more than 100 hours is required for 50% conversion with B_2F_4 (28). On the assumption that the reaction proceeds via a donor-acceptor interaction between the olefin and the boron compound, this result

is generally consistent with the greater Lewis acidity of boron chlorides as compared to the corresponding fluorides (29).

(2) The available data suggest that ethylene is the most reactive, or certainly among the most reactive, of olefins whose reaction with B_2Cl_4 has been investigated. Substituents on the doubly bonded carbon atoms almost invariably reduce the rate of addition. The preparative study of Ceron *et al.* (23) indicates, for example, that reactivity towards B_2Cl_4 decreases in the order ethylene > propene > 2-butene. Zeldin has observed that under comparable conditions ($0^\circ C$, olefin/ B_2Cl_4 ratio 4.7) *trans*-2-butene undergoes complete addition in less than 1 hour, while *trans*-di-*tert*-butylethylene reacts to the extent of 3.3% in 1 hour and 19% in 7 hours. Steric inhibition by the bulkier substituents was suggested as a possible explanation of the reactivity difference. Styrene reacts somewhat less rapidly (73% in 1 hour at $0^\circ C$) than ethylene (96% in 1 hour at $0^\circ C$) under comparable conditions (117).

Other types of substituents such as halogens and dichloroboryl groups also reduce the reactivity of the double bond (23). Haloethylenes are particularly slow to react, although with these reagents more complex reactions occur (84, 88), as discussed in Section III,C.

Reaction with the nonconjugated diene 1,4-cyclohexadiene leads to the addition of either 1 or 2 moles of B_2Cl_4 , depending on the reactant ratio (91). Similarly, 1,3-butadiene apparently gives both 1:1 and 1:2 addition products (23), although these have not been characterized structurally. Reaction of B_2Cl_4 with excess cyclopentadiene or 1,3-cyclohexadiene led to consumption of the diboron reagent and apparent polymerization of the olefin (91). A 1:2 reaction product formulated as 1,2,3,4-tetrakis(dichloroboryl)-cyclohexane was obtained, however, from the reaction of 1,3-cyclohexadiene with a 3:1 excess of B_2Cl_4 (120).

Alkynes including acetylene (23), propyne (117), 2-butyne (90, 118), di-*tert*-butyl acetylene (117), and diphenylacetylene (112) react readily at room temperature with 1 mole of B_2Cl_4 to form the corresponding vicinal bis(dihaloboryl)olefins. In the case of acetylene, Urry (101) has mentioned the formation at $-80^\circ C$ of a solid complex from which the reagents can be recovered and which slowly reacts to form the 1:1 diboration product. Addition of a second mole of B_2Cl_4 to the olefinic 1:1 addition product has been described only in the case of acetylene. The product, 1,1,2,2-tetrakis(dichloroboryl)ethane is a solid, m.p. 29° – $30^\circ C$, stable to $200^\circ C$ and monomeric in the vapor (24). Addition of B_2F_4 to acetylene in 1:1 ratio has been

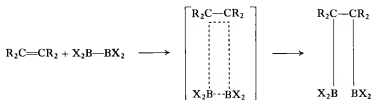
observed under forcing conditions (120° – 140° C, initial pressure ~ 7 atm.), while 2:1 addition does not occur (23). However, 1,1,2,2-tetrakis(difluoroboryl)ethane has been prepared indirectly by a halogen exchange reaction between $C_2H_2(BCl_2)_4$ and B_2F_4 (50).

The lack of reactivity of 1,2-bis(dichloroboryl)ethane toward addition of a second molecule of B_2Cl_4 may be attributable to the electron-withdrawing effect of the two dichloroboryl groups. It is of interest that the presence of a single BCl_2 group has much less effect. Thus, when $C_2H_3BCl_2$ is treated with B_2Cl_4 in a sealed tube at 35° C, half of the vinyl compound is converted to the saturated products in about 5 minutes, a rate which is significantly faster than the addition to *tert*-butyl ethylene under the same conditions. The corresponding reactions of the bis(dichloroboryl)ethylenes require 5 and 7 days for the *trans* and *cis* isomers, respectively (28).

B. Stereochemistry of the Addition Reaction

The stereochemical course of the addition of B_2Cl_4 to olefins and acetylenes has been studied by several groups (27, 90, 91, 118). As summarized in Table I, these investigations have, with a single exception, indicated that *cis* addition occurs.

At least three modes of addition can be postulated in these reactions (91). The most commonly suggested pathway involves interaction of the olefinic π -electron system with what may be viewed as the vacant π -system of the diboron compound. This four-center pathway would be expected to lead



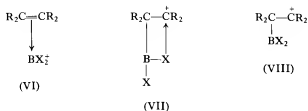
to *cis* addition, as is usually observed. It may be noted that, as commonly visualized, this process involves distortion of the conformation of the diboron molecule from the skewed configuration present in the liquid. Evidence for formation of identifiable π -complexes of the type postulated as intermediates is meager. Nevertheless, it appears that stabilization of B_2Cl_4 against thermal decomposition occurs in the presence of some olefins, even when the rate of addition is very slow.

TABLE I
STEREOCHEMISTRY OF B_2Cl_4 ADDITION REACTION

Reagent	Product	Inferred stereo-chemistry	Method ^a	References
Cyclopentene	1,2-Bis(dichloroboryl) cyclopentane	<i>trans</i>	H; O to diol; GC identification	(91)
<i>trans</i> -2-Butene	<i>dl</i> -2,3-Bis(dichloroboryl) butane	<i>cis</i>	H; O to diol; GC identification; m.p. of bis(<i>p</i> -nitrobenzoate)	(90, 118)
<i>cis</i> -2-Butene	<i>meso</i> -2,3-Bis(dichloroboryl)butane	<i>cis</i>		
Cyclohexene	<i>cis</i> -Bis-(dichloroboryl)-cyclohexane	<i>cis</i>	H; O to diol; m.p. of diol and bis(<i>p</i> -nitrobenzoate)	(118)
Acetylene	<i>cis</i> -1,2-Bis(dichloroboryl)ethylene	<i>cis</i>	Comparison of IR and Raman spectrum	(90)
			Photochemical isomerization; IR; ammoniacal silver cleavage	(27)
2-Butyne	<i>cis</i> -2,3-Bis(dichloroboryl)2-butene	<i>cis</i>	H; GC identification of olefin	(118)
Norbornylene	$C_7H_{10} \cdot B_2Cl_4$	<i>cis</i>	H; O; m.p. of <i>cis-exo</i> -2,3-norbornadiol	(117)

^a H, hydrolysis; O, oxidation; GC, gas chromatography; IR, infrared spectrum.

A reaction pathway involving heterolytic cleavage of the B—B bond might be expected to yield *trans* addition products if intermediates such as a coordinated boronium ion (VI) or a coordinatively stabilized carbonium ion (VII) were involved or nonspecific addition if a carbonium ion intermediate such as (VIII) were produced. The formally similar electrophilic addition of halogen to simple olefins is, of course, well known to lead to



trans addition. The effects of substituents on the rate of bromination of olefins do not parallel those observed in diboration reactions. Thus, electron-donating groups increase the reactivity of olefins toward halogens but the same groups apparently diminish reactivity toward B_2Cl_4 . On the other hand, halogen substitution on the olefinic carbon reduces the rate of both reactions. As previously mentioned, styrene reacts with B_2Cl_4 more slowly than does ethylene. It is apparent that the diboration reaction offers a prospect for more detailed kinetic and mechanistic studies.

A third mechanistic possibility involves homolytic cleavage of the boron-boron bond and attack on the olefin by dihaloboryl radicals. Such a process would most probably lead to nonstereospecific addition.

Demonstration of *cis* addition with acetylene is unequivocal, in that the stereochemistry of the resulting bis(dihaloboryl)ethylene has been shown directly by spectroscopic evidence (90) and by conversion of the initially produced *cis* isomer to the *trans* compound by photochemical isomerization (27). Stereochemical inferences in the olefin addition reactions are based on the assumption that hydrolysis and oxidation of the bis(boryl) compounds to the corresponding diols occurs with retention of configuration, as is the case in closely related systems (19). The NMR spectrum of the addition product of B_2Cl_4 with 1,3-cyclohexadiene is also consistent with *cis* addition (120).

Reaction of B_2Cl_4 with norbornylene gave a product from which *cis*-*exo*-2,3-norbornadiol was isolated after hydrolysis and alkaline peroxide oxidation, suggesting that stereospecific *cis* addition occurs. It was proposed that the preference for *exo* addition results from sterically preferred attack from above the plane of the ring (117).



It is of interest in connection with stereochemical investigations in these organoboron systems to note that protonolysis of *cis*- $Cl_2BCH=CHBCl_2$ with glacial CH_3COOD at $80^\circ C$ gave a mixture of *cis*- and *trans*- $C_2H_2D_2$. Thus, alkaline hydrolysis or reductive cleavage with ammoniacal silver oxide appears to be better suited to elucidation of stereochemistry in this type of organoboron derivative (27).

C. Reactions with Haloolefins

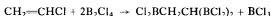
The presence of halogen substituents on an unsaturated carbon atom greatly reduces the reactivity of the carbon-carbon double bond toward addition of a diboron tetrahalide. Schlesinger and his co-workers reported that they observed no indication of "adduct" formation by B_2Cl_4 with vinyl chloride, vinyl fluoride, 1,1-difluoroethylene, 1,2-dichloroethylene, or tetrafluoroethylene. Insofar as investigated, these haloolefins were equally inert toward B_2F_4 (23).

In a study of the B_2Cl_4 -trichloroethylene system, no isolable adduct was obtainable and all the haloolefin could be recovered upon treatment of the reaction mixture with excess ammonia to remove the boron halide (35). It was reported that peaks attributable to an addition product and to an intermediate compound retaining the double bond were observed in the proton NMR spectrum, but later workers (28, 84, 117) were unable to verify this finding.

Although addition products were not isolated in these studies, it was observed that the formation of colored subchlorides arising from the decomposition of B_2Cl_4 is markedly reduced in mixtures of the subhalide with haloolefins (23). The decomposition of B_2Cl_4 occurs readily at room temperature or below in the pure liquid or in solutions in inert solvents such as hexane or ethyl chloride (Section II,C). Solutions in many haloolefins, however, may remain colorless for months to years at room temperature or above. Thus, the presence of the haloolefin has been considered to stabilize B_2Cl_4 , possibly through formation of a complex involving the π -system of the olefin and the vacant orbitals of the diboron compound (101).

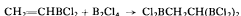
While it is clear that many haloolefins inhibit the disproportionation of B_2Cl_4 , early workers noted the formation of BCl_3 in mixtures of haloethylenes with B_2Cl_4 even though no color developed in these systems (92). This observation may be understood in the light of recent studies (88) which have shown that haloolefins are in fact not unreactive toward diboron tetrahalides.

Reinvestigation of the vinyl chloride- B_2Cl_4 system demonstrated that the reaction occurs slowly at room temperature in the absence of solvent in a 1:2 ratio.

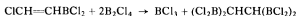


About half of the olefin is consumed in 5 days, during which time the reaction mixture remains colorless. The product, 1,1,2-tris(dichloroboryl)

ethane, is identical to that obtained from the addition of B_2Cl_4 to dichlorovinylborane.



Similarly, dichloro-2-chlorovinylborane yields 1,1,2-tetrakis(dichloroboryl)ethane, which may also be obtained by the addition of two moles of B_2Cl_4 to acetylene.

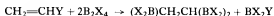


Similar reactions occur between boron subhalides and a number of chloro- and bromoolefins. The halogen originally present in the olefin appears, in differing amounts, as boron-bonded halogen in the addition product and as boron trihalide.

The reaction of the subhalides with haloethylenes apparently proceeds via a stepwise addition-elimination process. For a vinyl halide, this may be summarized as follows:

- (a) $CH_2=CHY + B_2X_4 \rightarrow (X_2B)CH_2CHY(BX_2)$
- (b) $(X_2B)CH_2CHY(BX_2) \rightarrow CH_2=CHBX_2 + BX_2Y$
- (c) $CH_2=CHBX_2 + B_2X_4 \rightarrow (X_2B)CH_2CH(BX_2)_2$

The overall reaction is thus



Redistribution of halogen substituents on boron may, of course, occur at any stage, thus complicating the product array, while the relative rates of the steps in the above sequence may differ for different X and Y. Thus, in the vinyl bromide- B_2Cl_4 system, an unstable saturated intermediate corresponding to the product in (a) was demonstrated by NMR spectroscopy and shown to decompose at room temperature to yield boron trihalide and vinylboron dihalide. No intermediates were noted in the reaction of vinyl chloride with B_2Cl_4 . On the other hand, significant accumulation of a vinylboron intermediate was observed in the vinyl bromide- B_2F_4 system.

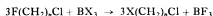
More highly chlorinated olefins are much less reactive toward B_2Cl_4 than is vinyl chloride, although addition products could be obtained after prolonged heating of the reaction mixtures at 100°C.

Vinyl fluoride undergoes halogen exchange with B_2Cl_4 to form vinyl chloride and fluorochloroboron derivatives (84). Simultaneously, but more slowly, the vinyl chloride is consumed by the reaction previously described to form 1,1,2-tris(dichloroboryl)ethane. The fluorine originally present in

the olefin appears principally as BF_3 in the final products of the reaction. Vinylidene fluoride is converted quantitatively over a period of a few days at room temperature to 1-chloro-1-fluoroethylene, which is apparently resistant both to further exchange and to reaction with the mixture of chlorofluorodiborons formed in the initial exchange reaction. In contrast, trifluoroethylene reacts with B_2Cl_4 to produce halovinylboron halides. The principal product, obtained in 50% yield, is dichloro-2,2-difluorovinylborane. Although the mechanism by which this product is formed has not been elucidated, it is probable that an addition-elimination is involved and that the compound is thus analogous to the unsaturated intermediates observed in reactions of the subhalides with vinyl bromide. A further product of the reaction with trifluoroethylene is a mixture of *cis*- and *trans*-dichloro(2-chloro-2-fluorovinyl)borane, which most probably arises from a halogen exchange reaction like that noted with vinylidene fluoride (84).

Fluoropropenes appear to react with B_2Cl_4 principally by halogen exchange which involves fluorine atoms on both sp^2 and sp^3 carbon (87). Thus, 2-fluoropropene is converted quantitatively in a few minutes at room temperature to 2-chloropropene, while *trans*-1,3,3,3-tetrafluoropropane reacts with an equimolar quantity of B_2Cl_4 to yield B_2F_4 and the corresponding tetrachloropropene. With 3,3,3-trifluoropropene, the rearranged product, 1,1,3-trichloropropene, is obtained. Interestingly, 2,3,3,3-tetrafluoropropene does not react with B_2Cl_4 at room temperature over a period of a month or more.

Similar halogen exchange reactions are shown by most of these fluoroolefins with BCl_3 , but at a much slower rate. Vinyl fluoride, for example, is completely converted to vinyl chloride in 5 days at room temperature in a 1:1 mixture with B_2Cl_4 . Under comparable conditions, only 40% reaction occurred in 9 weeks with BCl_3 (84). Similar halogen exchange reactions between boron halides and saturated organic fluorides have been noted by Olah and Kuhn (82).



Allyl fluoride is also reported to undergo halogen exchange with B_2Cl_4 (*vide infra*).

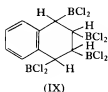
Haloolefins in which the halogen is bonded to a saturated carbon atom undergo the "normal" addition reaction, although the stability of the addition product may be low. Reaction of allyl chloride with B_2Cl_4 gives a

1:1 addition product which decomposes above -45°C with the formation of BCl_3 and involatile products. Although β -elimination of chlorine as BCl_3 might be anticipated in this reaction, it was reported on the basis of hydrolytic data that the C—Cl linkage of the allyl chloride was not affected during the reaction. The product from allyl chloride and B_2F_4 was even less stable than that obtained from the subchloride. When the halogen is more remote from the double bond, and thus from the boron atoms in the addition product, products are more stable. Thus, 1:1 compounds were obtained from both B_2Cl_4 and B_2F_4 with 4-chloro-1-butene (23).

Excess allyl fluoride is reported to react vigorously with B_2Cl_4 at -80°C to produce a product mixture including BCl_3 , BF_3 , B_2F_4 , and allyl chloride (23). The reaction is thus similar to the B_2Cl_4 -fluoroolefin reactions mentioned previously.

D. Reactions with Aromatic Hydrocarbons

Relatively little is known of the reactions of diboron tetrahalides with aromatics apart from a study by Fox and Wartik (39) of the interaction of B_2Cl_4 with benzene and naphthalene. With the former, dichlorophenylborane was obtained in high yield after long reaction times. With naphthalene, immediate formation of a loose complex was suggested by the formation of a bright yellow color. The reagents could be recovered from this complex by distillation, but after about 2 weeks at room temperature a product formulated as 1,2,3,4-tetrakis(dichloroboryl)tetralin (IX) was obtained.

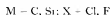


The NMR spectrum of this product is in agreement with the proposed structure, and suggests that the reaction yields a single isomer, formed by cis addition of B_2Cl_4 to the double bonds of the conjugated system of one ring, in which the BCl_2 groups occupy either *a-e-e-a* or *e-a-a-e* positions. The NMR and IR spectra suggest a marked structural similarity to the 1:2 addition product of 1,3-cyclohexadiene with B_2Cl_4 (120).

E. Reactions with Unsaturated Organometallic Derivatives

Reactions of B_2F_4 with diphenylmercury and tetravinyltin have been mentioned previously (Section I,A). No evidence was obtained for addition to the double bonds of the organometallic reagent in these studies.

Reactions of B_2F_4 and B_2Cl_4 with a number of monovinyl derivatives of boron, carbon, silicon, germanium, and tin have been investigated (28). Smooth addition was found in each case:



With divinyltin dichloride, evidence was obtained suggesting formation of both 1:1 and 1:2 addition products with B_2Cl_4 . Reaction of B_2Cl_4 with vinylsilane and vinyltrifluorosilane involves addition, accompanied by some transfer of hydride and fluoride to boron, suggesting that the addition products were mixtures resulting from redistribution of substituents between boron and silicon. Halide-hydride interchange of this type has been observed in reactions of trialkylsilanes with both B_2F_4 and B_2Cl_4 (86). The halogen exchange with trifluorovinylsilane is reminiscent of the reactions of B_2Cl_4 with allyl fluoride and fluoropropenes mentioned above (Section III,C).

These addition reactions, like the similar additions to olefins, can conveniently be studied by proton NMR spectroscopy. The resonances of the vinylic reagents are well separated from those of the saturated products, and measurements of intensities in the two regions provides a convenient measure of the extent to which the reaction has proceeded. The addition products of monovinyl derivatives are substituted ethanes of the $CH_2-XCHXY$ type, in which the methylene protons are geometrically non-equivalent, although the chemical shift differences may be vanishingly small. Spectra obtained may thus vary from the simple AX_2 type to more complex ABC patterns.

Measurement of the rate at which the olefinic resonances disappear and the peaks due to the saturated addition products appear permits a rough

comparison of the relative reactivities. Table II gives the times required for conversion of half of the vinyl compound to addition product at 35°C for a number of unsaturated derivatives.

TABLE II
REACTIVITY OF VINYL DERIVATIVES WITH B₂X₄

Compound	Boron halide	Reaction half-time ^a
C ₂ H ₃ Si(CH ₃) ₃	B ₂ Cl ₄	<5 min
C ₂ H ₃ Si(CH ₃) ₃	B ₂ F ₄	<20 hr
C ₂ H ₃ BCl ₂	B ₂ Cl ₄	~5 min
C ₂ H ₃ BF ₂	B ₂ F ₄	100 hr
C ₂ H ₃ SnCl ₃	B ₂ Cl ₄	~5 min
C ₂ H ₃ C(CH ₃) ₃	B ₂ Cl ₄	30 min
C ₂ H ₃ C(CH ₃) ₃	B ₂ F ₄	>100 hr
C ₂ H ₃ GeCl ₃	B ₂ Cl ₄	160 min
C ₂ H ₃ SiCl ₃	B ₂ Cl ₄	55 min
C ₂ H ₃ SiF ₃	B ₂ F ₄	No reaction
C ₂ H ₃ Cl	B ₂ Cl ₄	5.7 days ^{b,c}
<i>trans</i> -Cl ₂ BCH=CHBCl ₂	B ₂ Cl ₄	5 days
<i>cis</i> -Cl ₂ BCH=CHBCl ₂	B ₂ Cl ₄	7 days
<i>trans</i> -ClCH=CHBCl ₂	B ₂ Cl ₄	~80 days ^{c,d}

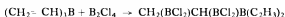
^a By NMR. Time required for conversion of half of the vinyl compound to saturated products. Reactant ratios 1:1, sealed tubes, 35°C (28).

^b Ratio of C₂H₃Cl: B₂Cl₄, 1:2

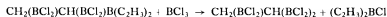
^c Reaction is not a simple addition; see Section III,C.

^d At 25°C.

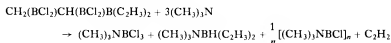
Addition of B₂Cl₄ to one of the double bonds in trivinylborane was reported by Holliday and Ottley (58).



The product reacted with BCl₃ to yield 1,1,2-tris(dichloroboryl)ethane and chlorodivinyborane.



With excess trimethylamine in a sealed tube at 120°C, the addition product underwent a reaction formulated as



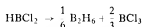
Kotz and Post have reported an interesting reaction of B_2Cl_4 with ferrocene, in which the principal products are BCl_3 , hydrogen, and dichloroferrocenylborane (61, 62). Traces of dichloroborane were obtained, and this compound was found to react also with ferrocene to yield hydrogen, dichloroferrocenylborane, and some B_2H_6 . These results were interpreted in terms of an initial reaction of B_2Cl_4 with ferrocene.



The dichloroborane produced in this reaction may react with more ferrocene



or may disproportionate (64).



The hydrogen produced in the reaction of ferrocene with $HBCl_2$ can react with B_2Cl_4 to give additional $HBCl_2$ which can react with ferrocene to regenerate H_2 and continue the cycle.

Dichloroferrocenylborane is also produced by the reaction of BCl_3 with ferrocene, albeit at a much slower rate. The difference in reactivity may be attributable to the greater ability of B_2Cl_4 to form a π -complex, analogous to the tetracyanoethylene-ferrocene complex (89) or may reflect the importance of the $HBCl_2$ -ferrocene reaction. Neither B_2F_4 , BF_3 , nor HBF_2 appears to react with ferrocene (62).

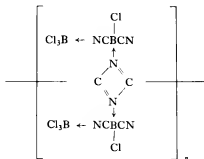
The reaction of B_2Cl_4 with ferrocene is of interest in comparison to the reaction of the halide with benzene which, as noted previously, also reacts by substitution and does not undergo an olefin-like diboration (39).

F. Reactions with Other Unsaturated Molecules

There is no clear evidence for formation of stable bis(boryl) derivatives from the interaction of diboron tetrahalides with molecules containing multiple bonds other than $C=C$ or $C\equiv C$. Such reactions as occur may in some cases involve initial diboration, but as they are of limited interest from the organometallic viewpoint, they will be mentioned only briefly.

Carbon monoxide, carbon dioxide, and sulfur dioxide are unreactive toward B_2Cl_4 at room temperature. Nitric oxide gives at $-78^\circ C$ a green solid product of composition B_2Cl_4NO which decomposes at $-40^\circ C$ with the evolution of BCl_3 . Addition to the NO molecule has been suggested,

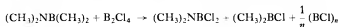
although it is not known whether the B—B bond is intact in the low-temperature product. Addition to the oxygen molecule to form $\text{Cl}_2\text{BOOBCl}_2$ has been suggested as the initial step in the oxidation of B_2Cl_4 (55). Cyanogen reacts with B_2Cl_4 in 1.5:1 ratio to give a solid in which the absence of B—B bonds is indicated by failure to produce hydrogen on alkaline hydrolysis. Structure (X) was proposed (2). A possible alternative (67) would involve formation of B—C and B—N bonds by addition across the triple bond.



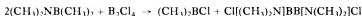
(X)

Acetone gives a 2:1 addition product with B_2Cl_4 at -23°C which decomposes at higher temperatures (66). Propionic acid reacts readily with B_2F_4 at 20°C , yielding hydrogen and difluoropropionyloxyborane (51).

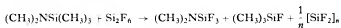
It has been suggested (57) that π -donation from an internal dative π -bond in dimethylaminodimethylborane can account for the formation of dichlorodimethylaminoborane and BCl polymer in the reaction with B_2Cl_4 .



The principal reaction in this system, however, is



A reaction similar to that cited above is observed in subvalent silicon chemistry (11)



although it is of interest that the sensitivity of halosilanes to base-catalyzed disproportionation is not shown by perhalodiborane(4) derivatives.

Co-condensation of B_2Cl_4 with carbon vapor afforded a mixture of compounds $CCl_n(BCl_2)_{4-n}$ ($n = 0, 1, 2$), while B_2F_4 gave species derived from C_1 , C_2 , and C_3 molecules, e.g., $C(BF_2)_4$, $(F_2B)_2C=C(BF_2)_2$, and $(F_2B)_2C=C=C(BF_2)_2$ (34).

IV

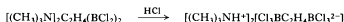
PROPERTIES OF SOME DIBORATION PRODUCTS

The addition of diboron tetrahalides to olefins provides a convenient route to vicinal bis(dihaloboryl)alkanes, which in general show most of the reactions to be expected of organoboron dihalides. The simplest member of this class of compounds, 1,2-bis(dichloroboryl)ethane is also the most extensively studied.

Thermal decomposition of $Cl_2BC_2H_4BCl_2$ is reportedly incomplete after 117 hours at $200^\circ C$, some 43% of the addition product being recoverable under these conditions along with BCl_3 and HCl . The marked sensitivity of both B_2Cl_4 and its reaction products to hydrolysis has been noted, so that formation of HCl in reactions of these compounds, particularly after prolonged reaction times, may arise at least in part from reaction with water absorbed from the reaction vessels. At $500^\circ C$, the compound is completely decomposed with the formation of hydrogen, methane, ethane, BCl_3 , and $(BCl)_n$ polymer (54).

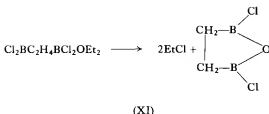
Like the parent subhalide, 1,2-bis(dichloroboryl)ethane may function as a dibasic Lewis acid, forming stable 1:2 complexes with trimethylamine (53) or dimethyl or diethyl ether (92).

The trimethylamine complex is stable to water, methanol, and hydrogen chloride at room temperature. Heating with HCl in a sealed tube leads to the uptake of two molecules of the hydrogen halide, suggesting formation of an ionic product (53).



Formation of a 1:1 diethyl etherate has been mentioned; this compound is said to decompose via elimination of ethyl chloride to form the heterocycle (XI) (101).

Reaction of trimethylamine with all four boron atoms of 1,2,4,5-tetrakis-(dichloroboryl)cyclohexane was observed by Saha *et al.* (91). With the

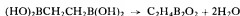


structurally similar 1:2 addition product from naphthalene, Fox and Wartik obtained uptake of only three molecules of base, and proposed that steric limitations account for the lack of further reactivity (39). Zeldin has reported a similar steric inhibition with diethyl ether as the base; only two ether molecules combined with the naphthalene addition product (117). The resulting complex rapidly eliminated all of the ethyl groups as ethyl chloride.

With excess dimethylamine, $\text{Cl}_2\text{BC}_2\text{H}_4\text{BCl}_2$ reacts incompletely (53) to give a volatile product formulated as $\text{B}_2(\text{NMe}_2)_4\text{C}_2\text{H}_4$. Ammonia and methylamine reacted similarly to give involatile products from which the expected ammonium salt could be sublimed. Methanolysis and hydrolysis gave the anticipated products.



The acid is reversibly dehydrated upon heating to 130°C .

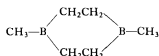


Oxidation of $\text{Cl}_2\text{BC}_2\text{H}_4\text{BCl}_2$ occurs slowly in dry air, vigorously in oxygen at temperatures above 0°C . At 0°C , reaction with oxygen occurs smoothly, with consumption of 1 mole of oxygen per mole of the addition product. Under these conditions, HCl , BCl_3 , and variable amounts of ethylene are the principal products. Possible mechanisms of this reaction have been discussed (53).

Treatment of bis(dichloroboryl)ethanes with dimethylzinc produces the corresponding bis(dimethylboryl) derivatives (23, 102). Several of these compounds have been characterized. Carefully purified samples of 1,2-bis(dimethylboryl)ethane decomposed slowly at room temperature or more rapidly at 100°C . The decomposition is apparently catalyzed by zinc compounds. The principal volatile products were trimethylborane and less volatile liquids for which structures such as (XII) and (XIII) were suggested, together with polymeric products (102).



(XII)

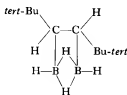


(XIII)

Reduction of the dihaloboryl compounds with lithium borohydride gives products whose stabilities show considerable dependence on structure. Urry *et al.* reported that reduction of 1,2-bis(dichloroboryl)ethane gave products that were unstable and difficult to purify (102). A liquid product, decomposing at -23° to -45°C with the liberation of diborane and non-condensables has subsequently been reported from this reaction (117, 119). When ethylene- d_4 was used to form the initial addition product, the diborane produced from the reduction product contained significant quantities of deuterium (117).

Lithium borohydride reduction of $\text{C}_{10}\text{H}_8(\text{BCl}_2)_4$, prepared from the interaction of B_2Cl_4 with naphthalene, gave a 28% yield of $\text{C}_{10}\text{H}_8(\text{BH}_2)_4$. Infrared and NMR evidence support a structure containing distinct BH_2 groups with no $\text{B}-\text{H}-\text{B}$ bridges (117, 119).

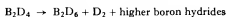
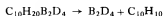
Reduction of the B_2Cl_4 addition products of *trans*-di-*tert*-butylethylene, *cis*-*tert*-butylmethylethylene, *trans*-2-butene, and norbornylene gave isolable hydrides stable *in vacuo* at temperatures ranging up to 200°C for the di-*tert*-butylethylene compound. In contrast to the naphthalene compound described above, these compounds show infrared bands characteristic of $\text{B}-\text{H}-\text{B}$ bridges (117). On the basis of infrared and NMR evidence, structure (XIV) was suggested for the compound derived from di-*tert*-



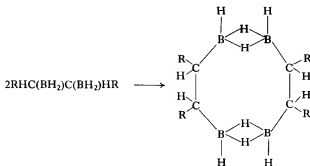
(XIV)

butylethylene and B_2Cl_4 . The compound yields diborane, *trans*-di-*tert*-butylethylene, noncondensables, and involatile solids on pyrolysis at 250° – 300°C . Interestingly, the diborane recovered from pyrolysis of

$C_{10}H_{20}B_2D_4$ was almost completely deuterated, suggesting a decomposition mechanism.

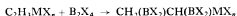


The possibility of intermolecular association was suggested for the hydrides derived from 2-butene and *tert*-butylmethylethylene. A high-field, tempera-



ture-dependence study of the ^{11}B NMR would be of considerable interest.

The 1:1 addition products obtained from vinylmetallic halides and diboron tetrahalides (28) are of structural interest by virtue of possessing not only vicinal bis(dihaloboryl) groupings but also a geminal arrangement of dihaloboryl and halometal groupings.

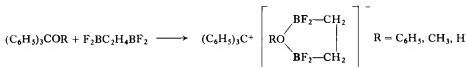


By analogy with β -haloorganoboranes, these compounds might be anticipated to undergo elimination reactions, at least in the thermodynamically more favorable cases. The compounds are in general stable at temperatures well in excess of $150^\circ C$, however. Similar thermal stability is shown by 1,1,2,2-tetrakis(dichloroboryl)ethane and its fluoro analog. The addition product of vinyltin trichloride and B_2Cl_4 undergoes a reductive elimination, slowly at room temperature and quantitatively at $100^\circ C$ in 16 hours.

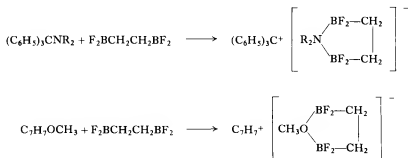


The difunctional Lewis acid character of 1,2-bis(dihaloboryl)ethylenes suggests the possibility that these compounds may behave as chelating acids

with bases containing two unshared electron pairs on the donor atom. The formation of such compounds has been observed with triphenylmethyl ethers and triphenylmethylcarbinol (10, 95). Formulation of the salts as



1:1 adducts was based on infrared evidence showing the presence of only four-coordinate boron. Similar products were obtained by reaction of the difunctional acid with triphenylmethylamines in methylene chloride or with 1,3,5-cycloheptatrienyl-7 methyl ether. In nonpolar solvents, the



triphenylmethylamines give unchelated 1:1 adducts, as does 1,3,5-cycloheptatrienyl-7-*N,N*-dimethylamine (9). A number of bases, such as dimethyl ether, tetrahydrofuran, diphenylcyclopropene, and pyridine *N*-oxide gave 2:1 adducts. Evidence for the operation of an authentic "chelate effect" was obtained from studies of the displacement of BF_3 from $(\text{C}_6\text{H}_5)_3\text{C}^+[\text{CH}_3\text{O} \cdot 2\text{BF}_3]^-$ by $\text{F}_2\text{BC}_2\text{H}_4\text{BF}_2$ (95).

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Organo-Transition Metal Chemistry— A Guide to the Literature 1950–1970

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A. Textbooks	274
B. Reviews	281
C. Primary Journals	285
D. Abstracting Journals and Information Retrieval	288
E. Conference Reports	290
F. Synthesis	293
G. Compound and Formula Registers	295
References	296
Appendix	297

The newcomer to organometallic chemistry, as to any other large branch of chemistry, may well find the superabundance of papers, review articles, bibliographies, and books, not to mention the never-ending flow of computer output and abstracting service products, confusing, to say the least. The vast majority of the literature in this area is the result of endeavors carried out in the last twenty years, and the Editors felt that a guide to the literature describing transition metal organometallics might be appropriate to this tenth volume of *Advances in Organometallic Chemistry*.

The large number of publications available—currently over 2500 new papers appear each year in this area—inevitably means that much of this new information remains unnoticed until reported more widely in the secondary accounts, such as the various annual surveys, which are necessarily selective. At an even later date, the more specialized reviews may include some references to the new work. Sufficiently interesting and important material may find its way into the more general surveys of chemical happenings, and eventually into textbooks, if the subject has sufficiently wide appeal.

In contrast, this guide, which does not claim completeness, takes the reader from the general to the specific, and covers in turn textbooks, both general and specialized, review articles, annual reports, the original literature, and conference reports and proceedings. A list of the most useful

reviews has also been compiled. As with other areas of chemistry, fashions change rapidly, and consequently a currently productive field of research may well be superseded by another within a few years. A detailed survey of general chemical literature is available which discusses at further length many of the points mentioned below (I).

A. Textbooks

Relatively few textbooks on organometallic chemistry are available, and with such a rapidly developing subject, these are invariably rendered somewhat out of date within a few years of publication.

In general texts on inorganic chemistry, the subject of transition metal organometallics is seldom well covered. An outstanding exception is the well-known and well-used book by Cotton and Wilkinson (A1), in the second edition of which two chapters succinctly relate the main principles, illustrated with a few well-chosen examples. Other texts, such as those mentioned below (A2-4), place rather less emphasis on this field.

- A1. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed. Wiley, New York, 1966. Probably the best general introduction to organo-transition metal chemistry. See Chapter 27 (pp. 719-760): Complexes of π -acceptor (π -acid) ligands; Chapter 28 (pp. 761-795): Organometallic compounds of transition metals.
- A2. C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Oxford University Press (Clarendon), London and New York, 1966. Another good introduction to this area in the context of inorganic chemistry. See Volume 2, Chapter 27 (pp. 327-368): Organometallic and related compounds.
- A3. P. J. Durrant and B. Durrant, "Introduction to Advanced Inorganic Chemistry," 2nd ed. Longmans, London, 1970. Chapter 27, pp. 1125-1196: The carbonyls, carbonyl hydrides, carbonyl halides, nitrosyls, and π -complexes of the transition metals. cursory survey of title topics.
- A4. H. J. Emeléus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," 3rd ed. Routledge & Kegan Paul, London, 1960. One of the first good expositions of modern inorganic chemistry. See pp. 252-313: Metal carbonyls and other π -bonded complexes.

Of the early accounts of organometallic chemistry which appeared in the first four decades of this century (for example, A5-11), the most comprehensive was that by Krause and von Grosse (A5), published in Germany in 1937. This scarce work has recently been reprinted, and is of interest largely to the historian, summarizing work on alkyls and aryls up to 1936. The section dealing with the transition metals is confined to some 35 out of 814 pages. Nevertheless, this book is particularly valuable as a source of early work on mercury and Main Group metals.

- A5. E. Krause and A. von Grosse, "Die Chemie der Metallorganischen Verbindungen." Bornträger, Berlin, 1937. Reprinted Dr. Martin Sändig oHG (1965). Mainly alkyls, transition metals covered on pp. 766–801. Does not mention, e.g., Zeise's salt.
- A6. J. Schmidt, "Organometallverbindungen." Wissenschaftliche Verlagsgesellschaft, Stuttgart, 1934.
- A7. E. Abderhalden, "Handbuch der biologischen Arbeitsmethoden." Urban & Schwarzenburg, Berlin and Vienna, 1929. Abt. 1, Teil 2, 2. Hälfte, Heft 4, E. Klärmann-Bloomfield: Darstellung metallorganischer Verbindungen.
- A8. J. Newton Friend, "A Textbook of Inorganic Chemistry." Griffin, London, 1928. Vol. 11, part 4, A. E. Goddard and D. Goddard: Organometallic Compounds of Se, Te, Cr and Pt.
- A9. R. Garzuly, "Organometalle, Sammlung chemischer und Chemische-technische Vorträge." Enke, Stuttgart, 1927.
- A10. J. Houben and V. Weil, ed., "Die Methoden der organischen Chemie." Thieme, Leipzig, 1924. Vol. 4, W. Schlenk: Organometallverbindungen.
- A11. J. W. Mellor, "Comprehensive Treatise of Inorganic and Theoretical Chemistry." Longmans, London, 1924. Vol. 5, pp. 950–962: The metal carbonyls.

After the well-known renaissance of organometallic chemistry which followed the discovery of ferrocene in 1950, the establishment of the basic principles, and the exploration of many facets of organo-transition metal chemistry finally resulted in the appearance of several texts devoted specifically to organometallics. The best known and most useful of these is the monograph of Coates, which first appeared in 1956. This volume of 197 pages was rapidly revised and expanded. The second edition was published only three years later, and the third edition became multi-authored and grew to two volumes, dealing with the Main Group elements, and Transition Metals, respectively (A12). This text represents a fairly detailed exposition of the subject, and newcomers to the area may find a condensed version (A13), concerned mainly with principles, to be more palatable, and to provide a more useful introduction to the subject.

Other books, similarly written at the undergraduate or first-year post-graduate level, are now appearing. These supplement the several bachelor degree or equivalent courses offered by the various educational establishments, and each of the texts listed below has an individual approach to the subject, which may be more or less acceptable to a particular course or reader (A14–20).

- A12. G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," 3rd ed. Methuen, London. Vol. 1, The Main Group Elements (1967); vol. 2, The Transition Elements (1968). Currently the best general introduction to organometallic chemistry, though necessarily a little dated. Originally published in 1956, written by G. E. Coates, with a second edition in 1960.

- A13. G. E. Coates, M. L. H. Green, P. Powell, and K. Wade, "Principles of Organometallic Chemistry." Methuen, London, 1968. Shorter edition of A12 above, mainly achieved by eliminating facts.
- A14. E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," Wiley, New York, 1957. The first text to deal specifically with modern organometallic chemistry. Chapter 10, pp. 231-274, Compounds of the transition metals. Also some discussion of metal carbonyls, pp. 313-319.
- A15. E. G. Rochow, "Organometallic Chemistry." Reinhold, New York, 1964. Slim paperback introduction, extremely readable, and containing many useful references.
- A16. P. L. Pauson, "Organometallic Chemistry." Arnold, London, 1967. Short introductory volume, written largely from an organic chemist's viewpoint.
- A17. O. Y. Okhlobystin, "A Third Chemistry: Organometallic Compounds." Nauka Press, Moscow, 1965. In Russian, for the nonspecialist.
- A18. J. J. Eisch, "The Chemistry of Organometallic Compounds—the Main Group Elements." Macmillan, New York, 1967. In spite of the title, contains some material on bonding in transition metal compounds.
- A19. R. B. King, "Transition Metal Organometallic Chemistry." Academic Press, New York, 1969. Introduction to major principles, with much descriptive material, arranged by Periodic Groups. Contains useful references, and problems designed to test assimilation of textual matter.
- A20. M. Tsutsui, M. N. Levy, A. Nakamura, M. Ichikawa, and K. Mori, "Introduction to Metal π -Complex Chemistry." Plenum, New York, 1970.

The area of organo-transition metal chemistry now has so many ramifications and applications that specialist books on a variety of topics have either appeared, or are being produced (A21-35). In the next few years, for example, one publisher will produce a series of texts covering the detailed organometallic chemistry of the transition elements.* Similar treatments covering many of the Main Group elements are also currently available, but do not come within the scope of this survey. However, no account of the literature of organometallic chemistry would be complete without a mention of the series edited by Nesmeyanov and Kocheshkov (A36), covering the practical aspects of the organic chemistry of many Main Group elements. A comparable series concerned with organo-transition metal chemistry has yet to appear.

- A21. N. A. Belozerskii, "Metal Carbonyls." Moscow, 1958. Russian. Surprisingly the only book devoted solely to the metal carbonyls, but generally inaccessible, and now considerably out of date.
- A22. A. D. Gel'man, "Complex Compounds of Platinum with Unsaturated Molecules." Soviet Academy of Sciences, Moscow, 1945. In Russian. An early account of olefin-platinum complexes, mainly centered about the author's studies.
- A23. E. O. Fischer and H. Werner, "Metal- π -Komplexe mit di- und oligo-olefinischen Liganden." Verlag Chemie, Weinheim, 1963.

* Added in proof: The first volumes on transition metals are: P. M. Maitlis, "Organic Chemistry of Palladium." Academic Press, New York. Vols. 1 and 2 (1971).

- A23a. E. O. Fischer and H. Werner, "Metal π -Complexes." Elsevier, Amsterdam, 1966. Vol. 1: Complexes with di- and oligo-olefinic ligands. English translation of A23 above, which, while partly updated, is now very much out of date.
- A24. P. Heimbach and R. Traummüller, "Chemie der Metall-Olefin-Komplexe." Verlag Chemie, Weinheim, 1970.
- A25. H. Zeiss, P. J. Wheatley, and H. J. S. Winkler, "Benzenoid Metal Complexes." Ronald Press, New York, 1966. Excellent account of the chemistry of arene-chromium complexes, now dated.
- A26. M. Rosenblum, "Chemistry of the Iron Group Metallocenes: Ferrocene, Ruthenocene, Osmocene." Wiley (Interscience), New York, 1965. Only vol. 1 published, which is an excellent introduction to the organic chemistry of ferrocene and its two congeners, but unfortunately not yet completed by the appearance of vol. 2.
- A27. H. J. de Liefde Meijer, M. J. Janssen, and G. J. M. van der Kerk, "Studies in the Organic Chemistry of Vanadium." Institute for Organic Chemistry TNO, Utrecht, 1963. Summary of authors' work on organovanadium chemistry.
- A28. R. Feld and P. L. Cowe, "The Organic Chemistry of Titanium." Butterworth, London, 1965. Summary of descriptive organo-titanium chemistry, including many references to patent literature; little theoretical treatment.
- A29. Houben-Weyl, "Methoden der organischen Chemie," 4th ed. Thieme, Stuttgart, 1970. Vol. 13, part 1: Metallorganische Verbindungen: Li, Na, K, Rb, Cs; Cu, Ag, Au.
- A30. C. W. Bird, "Transition Metal Intermediates in Organic Synthesis." Logos Press, London, 1967. Not very well produced account of title topic, suffering from too much descriptive detail with little rationalization of reactions described.
- A31. K. A. Andrianov, "Metalorganic Polymers." Wiley (Interscience), New York, 1965. Excellent account, but transition metals necessarily feature to only a small extent. Many references to Russian work in this area.
- A32. G. Henrici-Olivé and S. Olivé, "Polymerisation." Verlag Chemie, Weinheim, 1969. Excellent survey of theory and use of organo-transition metal catalysts for polymerization of organic monomers.
- A33. L. Reich and A. Schindler, "Polymerisation by Organometallic Compounds." Wiley, New York, 1966.
- A34. J. L. Harwood, "Industrial Applications of the Organometallic Compounds." Chapman & Hall, London, 1963. An expansion of fourteen articles appearing in *The Industrial Chemist* 1959–1960, dealing specifically with industrial chemistry and including an extensive compilation of the patent literature.
- A35. J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds." Academic Press, New York, 1970. Compendium of thermochemical data arranged by Periodic Group, but coverage of organotransition metal compounds limited by lack of data.
- A36. A. N. Nesmeyanov and K. A. Kocheshkov, eds., "Methods of Elemento-Organic Chemistry." North-Holland, Amsterdam, 1967. Extremely useful sources of preparative methods and properties, with extensive tabulations. Vol. 1, A. N. Nesmeyanov and R. A. Sokolik: The organic compounds of boron, aluminium, gallium, indium, and thallium. Vol. 2, S. T. Ioffe and A. N. Nesmeyanov: The organic compounds of magnesium, beryllium, calcium, strontium, and barium. Vol. 3, N. I. Sheverdina and K. A. Kocheshkov: The organic compounds of zinc and cadmium. Vol. 4, L. G. Makarova and A. N. Nesmeyanov: The organic compounds of mercury.

Another type of hardcover publication contains collections of articles centered around a particular theme (A37–43). Again of some historical

interest, the American Chemical Society monographs on coordination chemistry, published in 1956 (A37), and on organometallic chemistry, appearing in 1960 (A38), served to draw attention to, and to interest many people, including the author, in organometallic chemistry. More recently, other books have treated the influence of organometallics on organic synthesis (A39), or have described methods of characterization (A40) and experimental techniques (A41).

- A37. J. C. Bailar, ed., assisted by D. H. Busch, "The Chemistry of the Coordination Compounds." Reinhold, New York, 1956 (ACS Monograph 131). Valuable survey of the contemporary state of coordination chemistry, and of the early results on organometallic compounds, summarized in the chapters by:
- 37.1 B. E. Douglas: Coordination compounds of metal ions with olefins and olefin-like substances, pp. 487-508 (110).*
 - 37.2 J. A. Mattern and S. J. Gill: Metal carbonyls and nitrosyls, pp. 509-546 (153).
- A38. H. A. Zeiss, ed., "Organometallic Chemistry." Reinhold, New York, 1960 (ACS Monograph 147). Important collection of articles doing for organometallic chemistry what Bailar and Busch's book (A37 above) did for coordination chemistry four years previously. The whole contents are listed below, although not all relate to organo-transition metal chemistry:
- 38.1 J. W. Richardson: Carbon-metal bonding, pp. 1-35 (41).
 - 38.2 R. Huisgen: Benzyne chemistry, pp. 36-87 (125).
 - 38.3 H. D. Kaesz and F. G. A. Stone: Vinylmetallics, pp. 88-149 (154).
 - 38.4 H. C. Brown: Organoboranes, pp. 150-193 (103).
 - 38.5 K. Ziegler: Organo-aluminum compounds, pp. 194-269 (382).
 - 38.6 H. Gilman and H. J. S. Winkler: Organosilylmetallic chemistry, pp. 270-345 (185).
 - 38.7 P. L. Pauson: Cyclopentadienyl metal compounds, pp. 346-379 (222).
 - 38.8 H. Zeiss: Arene complexes of the transition metals, pp. 380-425 (128).
 - 38.9 G. E. Coates and F. Glockling: Transition metal alkyls and aryls, pp. 426-467 (122).
 - 38.10 J. Chatt, P. L. Pauson, and L. M. Venanzi: Metal carbonyls and related compounds, pp. 468-528 (312).
- A39. I. Wender and P. Pino, eds., "Organic Syntheses via Metal Carbonyls." Wiley (Interscience), New York, 1968. First volume of projected two-volume survey of title topic, containing good comprehensive summary of metal carbonyls, and the best accounts of acetylene-metal carbonyl interactions, among other contributions:
- 39.1 F. Calderazzo, R. Ercoli, and G. Natta: Metal carbonyls—preparation, structure and properties, pp. 1-272 (1410).
 - 39.2 W. Hübel: Organometallic derivatives from metal carbonyls and acetylene compounds, pp. 273-342 (146).
 - 39.3 C. Hoogzand and W. Hübel, Cyclic polymerisation of acetylenes by metal carbonyl compounds, pp. 343-371 (86).
 - 39.4 R. F. Heck: Organic syntheses via alkyl and acylcobalt tetracarbonyls, pp. 373-403 (32).

* Figures in parentheses indicate number of references quoted in each article.

- 39.5 A. Rosenthal and I. Wender: Reactions of nitrogen compounds, pp. 405–466 (124).
- A40. M. Tsutsui, ed., "Characterisation of Organometallic Compounds." Wiley (Interscience), New York. Vol. 1 (1969), vol. 2 (1971). Useful collection of articles describing application of various physical methods to the characterization of organometallic compounds, and covering both Main Group and Transition Metal derivatives. Volume 1 contains:
- 40.1 F. K. Cartledge and H. Gilman: Introduction to organometallic chemistry, pp. 1–33 (183).
 - 40.2 O. Schwarzkopf and F. Schwarzkopf: Chemical characterisation of organometallic compounds, pp. 35–72 (67).
 - 40.3 K. Nakamoto: Characterisation of organometallic compounds by infrared spectroscopy, pp. 73–135 (186).
 - 40.4 R. W. Kiser: Mass spectroscopy of organometallic compounds, pp. 137–211 (267).
 - 40.5 N. C. Baenziger: The determination of organometallic structures by X-ray diffraction, pp. 213–276 (280).
 - 40.6 R. Varma: Characterisation of metalloid and organometallic compounds by microwave spectroscopy, pp. 277–314 (73).
 - 40.7 R. H. Herber: Characterisation of organometallic compounds by Mössbauer spectroscopy, pp. 315–340 (46).
- Volume 2 contains:
- 40.8 R. G. Kidd: Nuclear magnetic resonance spectroscopy of organometallic compounds, pp. 373–437 (164).
 - 40.9 L. N. Mulay and J. T. Dehn: Magnetic susceptibility—characterisation and elucidation of bonding in organometallics, pp. 439–480 (43).
 - 40.10 F. J. Smentowski: Characterisation of organometallic compounds by electron spin resonance, pp. 481–651 (1236). Particularly useful for an extensive literature review. Mainly Main Group elements and anion radicals, but with important section on metallocenes.
 - 40.11 W. T. Reichle: Preparation, physical properties, and reactions of sigma-bonded organometallic compounds, pp. 653–826 (696). Main Group elements only.
- A41. D. B. Denny, ed., "Techniques and Methods of Organic and Organometallic Chemistry." Dekker, New York, 1969. The first volume of this series contains only one article of general interest:
- 41.1 A. C. Bond: High-vacuum techniques, pp. 33–50 (9).
- A42. W. O. George, ed., "Spectroscopic Methods in Organometallic Chemistry." Butterworth, London (1970).
- A43. E. I. Becker and M. Tsutsui, eds., "Organometallic Reactions." Wiley, New York. Vol. 1 (1970), vol. 2 (1970). This series contains detailed reviews of organometallic reactions, with discussions of mechanisms and experimental details. Volume 1 contains:
- 43.1 T. Mole: Redistribution reactions of organoaluminium reactions, pp. 1–54 (245).
 - 43.2 M. E. Vol'pin and V. B. Shur: Chemical fixation of molecular nitrogen, pp. 55–117 (118).
 - 43.3 L. G. Makarova: Reactions of organomercury compounds, Part 1, chapters 1–11, pp. 119–348 (882).

Volume 2 contains:

- 43.4 K. Moedritzer: The redistribution reaction, pp. 1-115 (495).
- 43.5 K. J. Irgolic and R. A. Zingaro: Reactions of organotellurium compounds, pp. 117-334 (307).
- 43.6 L. G. Makarova: Reactions of organomercury compounds, Part 2, chapters 12-17, pp. 335-423 (438).

Finally in this section should be mentioned a variety of authoritative treatises all relating ostensibly to a non-organometallic subject, but which may contain in one or two chapters, the contributions of organometallic chemistry to these particular areas (A44-56). Other sources include two collections of essays presented to G. Schwarzenbach (A57) and to H. J. Emeléus (A58), and a selection of the papers of A. N. Nesmeyanov (A59). The latter is chiefly of interest in the present context because of the early work on ferrocene that is reported.

- A44. S. Patai, ed., "The Chemistry of Alkenes." Interscience, New York.
Volume 1 (1964) contains an article by:
 - 44.1 M. Cais: Alkene complexes of some transition metals, pp. 335-385 (116).Volume 2 (edited by J. Zabicky, 1970) contains:
 - 44.2 J. F. Biellmann, H. Hemmer, and J. Levisalles: Alkene complexes of transition metals as reactive intermediates, pp. 215-265 (258).
- A45. V. Gutmann, ed., "Halogen Chemistry." Academic, New York, 1967.
Volume 3 contains an article by:
 - 45.1 F. Calderazzo: Halogeno-metal carbonyls and related compounds, 383-434 (173), which is an expansion of the appropriate part of article A39.1.
- A46. P. H. Plesch, ed., "Cationic Polymerisation and Related Complexes." Heffer, Cambridge, 1953, contains:
 - 46.1 J. Chatt: General chemistry of olefin complexes with metallic salts, pp. 40-56 (49), an early survey of this area.
- A47. J. Lewis and R. G. Wilkins, eds., "Modern Coordination Chemistry." Wiley (Interscience), New York, 1961, contains:
 - 47.1 F. A. Cotton: The infrared spectra of transition metal complexes, pp. 301-399 (222), with a section on metal carbonyls and cyclopentadienyls.
- A48. S. Coffey, ed., "Rodd's Chemistry of Carbon Compounds." Elsevier, Amsterdam, 1965. The coverage of organic compounds in the second edition results in undesirable restraints being set upon the surveys of organometallic compounds. Two of these which have appeared are:
 - 48.1 C. B. Milne and A. N. Wright: Aliphatic organometallic and organometalloidal compounds, vol. 1, part B, pp. 246-277.
 - 48.2 M. Green, G. R. Knox, and P. L. Pauson: Metal cyclopentadienyls and metallocenes, vol. 2, part A, pp. 124-148.
- A49. W. Baker and J. F. W. McOmie, eds., "Non-Benzenoid Aromatic Compounds." Wiley (Interscience), New York, 1959, contains:
 - 49.1 P. L. Pauson: Compounds derived from cyclopentadiene, pp. 107-140a (197) an account of metal cyclopentadienyls, and the organic chemistry of ferrocene.
- A50. G. A. Olah, ed., "Friedel-Crafts and Related Reactions." Wiley (Interscience), New York, 1965.

Volume 4 contains:

- 50.1 K. Hafner and K. L. Moritz: Reactions of non-benzenoid aromatics, pp. 127–183 (218). Includes ferrocenes, fulvenes, azulenes, etc.
- A51. R. N. Grimes, "Carboranes." Academic Press, New York, 1970. Chapter 9, Section 5, pp. 207–232: Carborane-transition metal π -complexes.
- A52. A. Schönberg, G. O. Schenk, and O.-A. Neumüller, "Preparative Organic Photochemistry," 2nd ed. Springer, Berlin, 1968. Chapter 45, pp. 459–470: Photochemical formation and reactions of organometallic compounds.
- A53. M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds." Academic Press, New York, 1967. Chapter 2, pp. 88–121: The cyclobutadiene-metal complexes.
- A54. F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions." Wiley, New York, 1958. Chapter 8, pp. 332–367: Catalytic effects of coordination compounds (105). This section was considerably expanded in the second edition (1967) as Chapter 7, pp. 526–627: Reactions of transition metal organometallics (250).
- A55. P. H. Emmett, ed., "Catalysis." Reinhold, New York.

Volume 5 (1957) contains important contributions by:

- 55.1 M. Orchin and I. Wender: Reactions of carbon monoxide, pp. 1–72 (141).
- 55.2 I. Wender, H. W. Sternberg, and M. Orchin: The oxo reaction, pp. 73–130 (100).
- A56. D. M. Adams, "Metal-Ligand and Related Vibrations." Arnold, London (1967). Of particular relevance to organometallic chemists are:
Chapter 1, sections 1–2: Transition metal hydrides, pp. 1–8, tables 1.1–1.10.
Chapter 3, sections 1–8: Metal-carbon frequencies in carbonyls and cyanides, pp. 84–111, 118–119, tables 3.1–3.20.
Chapter 4, section A: Metal-carbon and related frequencies in alkyl, aryl and π -bonded compounds, pp. 182–198, tables 4.1–4.18.
- A57. W. Schneider, G. Anderegg, and R. Gut, eds., "Essays in Coordination Chemistry" (dedicated to Gerold Schwarzenbach), *Experientia Supplementum IX*. Birkhäuser, Basel, 1964, containing articles by:
57.1 R. Mason and G. Wilkinson: Structure and bonding in transition metal complexes of some cyclic unsaturated ligands, pp. 233–239 (15).
57.2 H. P. Fritz: Spin-spin-kopplungen zwischen Protonen und Übergangsmetallen in Komplexen, pp. 250–258 (27).
57.3 E. O. Fischer and M. Herberhold: Photochemische Substitutionsreaktionen an Cyclopentadienyl-mangan-tricarbonyl, pp. 259–305 (75).
- A58. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, eds., "New Pathways in Inorganic Chemistry." Cambridge Univ. Press, London and New York (1968) contains:
58.1 H. C. Clark: Organometallic cations, pp. 1–13 (36).
58.2 F. G. A. Stone: Transition metal derivatives of silicon, germanium, tin and lead, pp. 283–302 (87).
- A59. A. N. Nesmeyanov, "Selected Works in Organic Chemistry." English translation issued by Pergamon, London (1963).

B. Reviews

Scientific publications double their number in a period estimated at between 8 to 10 years, which means that the practising chemist finds

keeping up with the literature becomes ever more time-consuming. Consequently, critical accounts which enable the essentials of various subjects to be rapidly assimilated are to be welcomed. Cahn has stated (2) that "reviews can usefully proliferate unrestrained, for they are needed at all levels," and this advice has resulted in a rapid increase in the numbers of titles of the type *Advances in . . .* or *Progress in . . .* In addition, the well-established review journals have generally increased in size.

Organometallic chemistry is well served by specialist publications of this type. Originally developing as a branch of inorganic chemistry, it was only natural that the two series *Advances in Inorganic Chemistry and Radiochemistry* (B1) and *Progress in Inorganic Chemistry* (B2) should initially attract articles on transition metal organometallics. Five years later, the present series was initiated, and ten volumes have now been published in the relatively short period of seven years (B3). The subject acquired its own review journal, *Organometallic Chemistry Reviews* (B4) in 1966. Details of individual reviews in these volumes are incorporated into the Appendix.

- B1. H. J. Emeléus and A. G. Sharpe, eds., "Advances in Inorganic Chemistry and Radiochemistry." Academic, New York, vols. 1 (1959), 2 (1960), 3 (1961), 4 (1962), 5 (1963), 6 (1964), 7 (1965), 8 (1966), 9 (1966), 10 (1967), 11 (1968), 12 (1969), 13 (1970)†.*
- B2. F. A. Cotton, ed., "Progress in Inorganic Chemistry." Interscience, New York, vols. 1 (1959), 2 (1960), 3 (1962), 4 (1962), 5 (1963), 6 (1964), 7 (1966), 8 (1967), 9 (1968), 10 (1968); ed. S. J. Lippard, vols. 11 (1970), 12 (1970), 13 (1970), 14 (1971).†
- B3. F. G. A. Stone and R. West, eds., "Advances in Organometallic Chemistry." Academic, New York, vols. 1 (1964), 2 (1964), 3 (1965), 4 (1966), 5 (1967), 6 (1968), 7 (1968), 8 (1970), 9 (1971), 10 (1972).†
- B4. *Organometallic Chemistry Reviews*, Elsevier, Amsterdam, vols. 1, 2 (1966-1967); Series A, Subject Reviews, vols. 3-8 (1968-1971). Beginning in 1972, this review journal will become part of the *Journal of Organometallic Chemistry*.

The research chemist likes to read not only about the specialized topics which interest him in detail, but also of the general chemical highlights of the preceding year. Since 1904, the Chemical Society's *Annual Reports* (B5) have covered, selectively, developments on an annual basis. Surveys of work on transition metal carbonyls and nitrosyls appeared at irregular intervals until 1955, after which time a new section on "Transition Elements" included an annual report on significant advances in this area. Five years later, a subdivision entitled "Complexes" included the work on organo-transition metal compounds. A new chapter, "Transition Metal

* The dagger (†) indicates continuing series. Volume numbers and years given for guidance only.

Carbonyls and Related Compounds," appeared in 1965, and continues to describe the more important developments in this area.

However, the recent increase in literature has somewhat reduced the general utility of this series. To supplement this publication, the Society undertook to prepare a series of Specialist Reports (B6), and among the first of these to appear was *Spectroscopic Properties of Inorganic and Organometallic Compounds*, three volumes of which have now appeared. Other

TABLE I
SUBJECT BREAKDOWN OF REFERENCES QUOTED IN
Organometallic Chemistry Reviews, Section B

Subject	Year surveyed					
	1964	1965	1966	1967	1968 ^a	1969 ^a
Results of general interest	33	38	67	57	223	245
Lanthanides and actinides	4	7	8	6	3	18
Ti, Zr, Hf	19	21	41	56	56	74
V, Nb, Ta	17	10	12	22	27	44
Cr, Mo, W	77	97	130	137	320	291
Mn, Tc, Re ^b	74	71	68	94	211	187
Ferrocene	64	70	74	87	207	231
Fe, Ru, Os	83	121	103	139	230	222
Co, Rh, Ir	62	95	93	162	215	145
Ni, Pd, Pt	74	105	103	126	219	287
Cu, Ag, Au	10	6	17	16	34	41
Mixed metals	—	5	6	8	—	—
Structures	—	—	—	—	155	179
	517	646	722	910	1900	1964

^a Multi-authored.

^b Includes cymantrene $[\text{Mn}(\pi\text{-C}_5\text{H}_5)(\text{CO})_3]$ chemistry.

reports of this type, of interest to organometallic chemists, and which are imminent or planned include *Mass Spectrometry of Organic and Organometallic Compounds* and *Organometallic Chemistry*.

In 1965, the first of a series of *Annual Surveys of Organometallic Chemistry* was published. The first three volumes covered work reported in the years 1964–1966, after which the publication became multi-authored, and assumed the style of *Organometallic Chemistry Reviews*. It is now published under this title, termed Series B (B7). Table I, a subject breakdown of the Transition Metals section, shows the number of references appearing each

year over the past six years, and gives a good indication of the relative effort devoted to each area. The figures also reflect the rapid growth of the subject, although the sharp increase between 1967 and 1968 is due in part to the change to a multi-author format, with inevitable duplication of some references. This may occur when a particular paper refers to the chemistry of elements from more than one Periodic Group.

- B5. Annual Reports, The Chemical Society, London, vols. 1-63 (1904-1966); then divided into Sections A (Inorganic and Physical Chemistry) and B (Organic Chemistry), vols. 64-67 (1967-1970).†
- B6. Specialist Periodical Reports, The Chemical Society, London. At present these include:
 - 6.1 "Spectroscopic Properties of Inorganic and Organometallic Compounds," ed. N. N. Greenwood, vols. 1 (1968), 2 (1969), 3 (1970). Each volume surveys the literature of the year before publication, under seven main chapter headings: Nuclear magnetic resonance spectroscopy; Nuclear quadrupole resonance spectra; Electron spin resonance spectroscopy; Microwave spectroscopy; Vibrational spectra; Electronic spectra; and Mössbauer spectroscopy.
 - 6.2 "Mass Spectrometry of Organic and Organometallic Compounds," ed. D. H. Williams, vol. 1 (1971). Relevant to organometallic chemistry is: M. I. Bruce: Organometallic and coordination compounds, pp. 182-252 (466), covering the period 1968 through mid-1970.
 - 6.3 "Organometallic Chemistry," eds. E. W. Abel and F. G. A. Stone, vol. 1 to survey the literature of 1971.
- B7. R. B. King and D. Seyferth, eds., "Annual Survey of Organometallic Chemistry," Elsevier, Amsterdam, vols. 1 (1965), 2 (1966), 3 (1967). Each volume surveys the literature appearing in the previous year. The series then became *Organometallic Chemistry Reviews, Series B, Annual Surveys*, vols. 4 (1968), 5 (1969), 6 and 7 (1970), 8 and 9 (1971). Beginning in 1972, this publication will merge with the *Journal of Organometallic Chemistry*.

The most often consulted general review journals are probably *Quarterly Reviews* (B8), which now also contain all the major lectures delivered to the Chemical Society, and *Chemical Reviews* (B9). Also useful are *Angewandte Chemie* (also published in English translation) (B10), *Accounts of Chemical Research* (B11), and *Uspekhi Khimii* (available in English as *Russian Chemical Reviews*) (B12). The latter provides a good coverage of work reported from Eastern European countries.

- B8. *Quarterly Reviews*, The Chemical Society, London, vols. 1-24 (1947-1970).†
- B9. *Chemical Reviews*, The American Chemical Society, vols. 1-53 (1925-1953); annual volumes from vol. 54 (1954 ff).
- B10. *Angewandte Chemie*, Gesellschaft Deutsche Chemiker, vols. 1-82 (1889-1970);† English translation (*International Edition in English*), Verlag Chemie, Weinheim/Academic Press, New York, vols. 1-9 (1962-1970)† (with different pagination).

- B11. *Accounts of Chemical Research*, The American Chemical Society, vols. 1–3 (1968–1970).†
- B12. *Uspekhi Khimii*, Moscow, vols. 1–39 (1932–1970).† English translation (*Russian Chemical Reviews*) published since 1960 by the Chemical Society, London, vols. 29–39 (1960–1970)† (with different pagination).

Large numbers of review articles are now appearing, and the Appendix attempts to index many of these under headings which reflect their content. Included are articles concerned with organo-transition metal chemistry appearing in the various publications mentioned already, and others which have come to the author's notice. The list is not comprehensive, and it is hoped to update the list periodically. Other general surveys of related fields (bibliographies of reviews) include *Bibliography of Reviews in Chemistry* (for the years 1958–1962 only) (B13), and two similar compilations relating to organic chemistry (B14–15).

- B13. *Bibliography of Chemical Reviews*, Chemical Abstracts Service, (1958–1962). Collected abstracts of reviews, arranged by the usual *Chemical Abstracts* sections.
- B14. D. A. Lewis, ed., "Index of Reviews—Organic Chemistry." I.C.I. Ltd., Plastics Division, Welwyn Garden City, Herts., England, 1968, with supplements (1969 and 1970). This publication is being continued by the Chemical Society, London. The first volume (1971) is a cumulative volume covering the period to December 1970. Annual supplements with triennial cumulative volumes are planned.
- B15. N. Kharasch and W. Wolf (and E. C. P. Harrison for vol. 1 only), "Index to Reviews, Symposia Volumes and Monographs in Organic Chemistry." Pergamon, Oxford, vol. 1, period 1940–1960 (1962); vol. 2, period 1961–1962 (1964); vol. 3, period 1963–1964 (1966). This publication is not arranged by subject, but by journal, consequently being tedious to use.

C. Primary Journals

Original work is reported in the primary journals, which continue to proliferate. Many papers appear in the national chemical society journals of the United Kingdom, the United States, Germany, the U.S.S.R., and Japan, in which countries much organometallic chemistry originates. Organometallic chemistry also has its own journal, which started in 1963, and recently others concerned with the use of organometallics in synthesis have appeared (see Section F).

Particularly important are the various journals which publish short communications. These resulted from a need for a more rapid means of communication between scientists, as the time taken for longer and more detailed papers to be published generally became over six months. The most useful of these is *Chemical Communications* (originally part of the *Proceedings*

of the Chemical Society, started in 1957), alternatively called *Section D* of the Society's *Journal*. Similar commercial publications are *Tetrahedron Letters* and *Inorganic and Nuclear Chemistry Letters*. Several journals carry preliminary accounts of work in the form of Communications to the Editor, the most important of these being *Journal of the American Chemical Society*, *Journal of Organometallic Chemistry*, *Angewandte Chemie*, and *Izvestia*.

Although the number of chemical journals is now legion, a breakdown of the references quoted in the *Annual Surveys of Organometallic Chemistry* over the past six years shows that the majority of original work appears in relatively few journals, as is shown in Table II. As can be seen, a different

TABLE II

BREAKDOWN (BY JOURNAL) OF REFERENCES QUOTED IN *Organometallic Chemistry Reviews*, Section B (ORGANO-TRANSITION METAL CHEMISTRY)

Journal	Year surveyed						^b
	1964	1965	1966	1967	1968 ^a	1969 ^a	
<i>J. Amer. Chem. Soc.</i>	68	84	116	119	253	274	(164)
<i>J. Organometal. Chem.</i>	36	52	85	119	209	222	(155)
<i>Chem. Commun. (Proc. Chem. Soc.)</i>	(12)	51	85	106	258	207	(158)
<i>J. Chem. Soc. (A)</i>	39	67	54	91	248	178	(129)
<i>Inorg. Chem.</i>	64	80	70	89	189	174	(106)
%:	50.8	59.3	63.9	65.9	70.9	64.1	
<i>Angew. Chem.</i>	19	20	31	26	54	45	
<i>Chem. Ber.</i>	32	34	23	26	24	39	
<i>Z. Naturforsch. (B)</i>	28	27	18	28	28	19	
<i>Inorg. Chim. Acta</i>	^c	^c	^c	1	37	51	
<i>Bull. Chem. Soc. Jap.</i>	10	10	16	15	28	32	
<i>Dokl. Akad. Nauk SSSR</i>	6	7	5	3	12	18	
<i>Izv. Akad. Nauk SSSR, Ser. Khim.</i>	8	7	12	10	24	27	
<i>Aust. J. Chem.</i>		3	7	10	20	14	
<i>Can. J. Chem.</i>		2	4	5	14	21	
%:	23.9	19.5	18.1	15.6	14.8	16.2	
<i>Acta Crystallogr.</i>	5	9	3	4	23	23	
<i>Zh. Strukt. Khim.</i>				3	11	25	
<i>Inorg. Nucl. Chem. Lett.</i>		3	14	16	20	30	
<i>Tetrahedron Lett.</i>	9	15	10	13	18	17	
<i>Nature (London)</i>	10	5	9	3	7	1	
<i>Chem. Ind. (London)</i>	11	6	12	2	3	3	
<i>Z. Chem.</i>	4	1		3	2	7	

TABLE II—continued

Journal	Year surveyed						^b
	1964	1965	1966	1967	1968 ^a	1969 ^a	
<i>Zh. Obshch. Khim.</i>		2	4	5	2	5	
<i>J. Inorg. Nucl. Chem.</i>	14	7	9	9	12	14	
<i>Z. Anorg. Chem.</i>	9	13	10	13	9	14	
<i>Zh. Neorg. Khim.</i>		1	1	3	4	8	
<i>J. Chem. Soc. (C)</i>	^c	^c	3	5	7	7	
<i>J. Org. Chem.</i>	4	4	1	2	11	10	
<i>Tetrahedron</i>	1			1	1	5	
<i>Annalen</i>		3	1	1	2	16	
<i>J. Chem. Soc. (B)</i>	^c	^c	1		8	9	
<i>Trans. Faraday Soc.</i>		2	3	2	2		
<i>J. Chem. Phys.</i>	3	5	8	6	14	17	
<i>J. Phys. Chem.</i>	2	6	4	5	2	6	
<i>Z. Phys. Chem.</i>	2	1	1	1	2		
<i>J. Mol. Spectrosc.</i>	1	1	1	1		6	
<i>Spectrochim. Acta</i>	3	2	1	2	7	4	
%:	14.8	10.5	10.7	8.05	5.82	8.02	
<i>Acta Chem. Scand.</i>	2	2	1	1		7	
<i>Chim. Ind. (Milan)</i>	5	2	1	1	1	1	
<i>Gazz. Chim. Ital.</i>	5	1		5	6	4	
<i>C. R. Acad. Sci., Ser. C</i>	3	5	4	7	8	15	
<i>Bull. Soc. Chim. Fr.</i>			2	1	5	4	
<i>Helv. Chim. Acta</i>	8	2	1	5		11	
<i>Monatsh.</i>		1	2	1	7	8	
<i>Rec. Trav. Chim.</i>		1	1	8	4	3	
%:	5.34	2.49	1.87	3.65	1.90	3.22	
Others (No. of journals)	8 (7)	19 (13)	8 (7)	18 (12)	37 (26)	44 (30)	
	431	563	642	795	1633	1645	

^a Multi-authored, hence some duplication unavoidable.^b For 1969, figures in parentheses indicate actual number of relevant articles published in the five journals first listed.^c Not published.

distribution of papers results from the predominantly organic chemistry described for ferrocene (Table III). It is obvious that periodic scanning of even only twenty-five of the most popular journals, for example, is unlikely to result in much important work being missed.

Most of the organometallic articles in Russian primary journals appear in English translation, published by either the Chemical Society, London,

TABLE III

BREAKDOWN (BY JOURNAL) OF REFERENCES QUOTED IN *Organometallic Chemistry Reviews*,
Section B (FERROCENE CHEMISTRY)

Journal	Year surveyed					
	1964	1965	1966	1967	1968	1969
<i>J. Chem. Soc. (A)</i>	1	3		2		2
<i>J. Chem. Soc. (C)</i>	^a	^a	1	5	6	7
<i>Chem. Commun.</i>		1	3	3	4	8
<i>J. Amer. Chem. Soc.</i>	7	7	3	12	7	11
<i>Inorg. Chem.</i>	3				1	4
<i>J. Org. Chem.</i>	8	10	4	5	6	7
<i>J. Organometal. Chem.</i>	3	4	11	14	11	12
<i>Tetrahedron</i>	1		1		3	3
<i>Tetrahedron Lett.</i>	2	2	3	6	10	8
<i>Z. Naturforsch. (B)</i>	2	3	1	1	1	
<i>Z. Chem.</i>		1		1	3	1
<i>Dokl. Akad. Nauk SSSR</i>	4	8	4		17	10
<i>Izv. Akad. Nauk SSSR</i>		6	10	12	14	9
<i>Zh. Obshch. Khim.</i>	2		1	1	7	6
<i>J. Chem. Phys.</i>	1			3	1	2
<i>Acta Crystallogr.</i>	3	1	1	2		1
<i>Can. J. Chem.</i>	2			1	2	2
<i>Bull. Chem. Soc. Fr.</i>	1	1	3	2	4	7
<i>C. R. Acad. Sci., Ser. C</i>	3		5	1	6	8
<i>Monatsh.</i>	3	5	3	4	9	14
<i>Collect. Czech. Chem. Commun.</i>	1	2	3	2		3
<i>Chem. Zvesti</i>	1		1	1	2	4
<i>Bull. Chem. Soc. Jap.</i>	1	3	3		2	6
Others (No. of journals)	12 (10)	11 (11)	14 (11)	4 (4)	44 (27)	57 (45)
	<u>61</u>	<u>68</u>	<u>75</u>	<u>82</u>	<u>160</u>	<u>192</u>

^a Published as *J. Chem. Soc.*

or the Consultants Bureau, New York. Extensive descriptions of individual translation services which are available have been given in Bottle's book (1).

D. Abstracting Journals and Information Retrieval

Original papers are abstracted relatively soon after publication, and these summaries, which are often no more than the author's own abstracts which normally precede the main text of a paper, are published in the various abstracting journals. The most comprehensive and important of these is

Chemical Abstracts, started in 1907. Between 1950 and 1958, most papers dealing with organo-transition metal chemistry appeared in Sections 6 (Inorganic Chemistry) and 10 (Organic Chemistry). In 1959 (vol. 53), the latter Section was regrouped, and organometallic chemistry of transition elements generally appeared at the beginning of Section 10G (Heterocyclic Compounds), as well as in Section 6, which remained unchanged. Another reorganization in 1962 (vol. 56) resulted in the majority of these papers appearing in Sections 8 (Crystallization and Crystal Structure), 14 (Inorganic Chemicals and Reactions), and 33 (Organometallic and Organometalloidal Compounds), the last section being renumbered 39 in the following year (vol. 58). In 1967 (vol. 66), the current system was introduced, the Sections being renumbered as 29 (previously 39), 70 (8), and 78 (14), although their scope was largely unaltered. Since this time also, abstracts have been individually numbered, which while resulting in six-figure numbers (e.g., up to 137183 in vol. 73), is more convenient than the earlier system of numbering columns.

Other major national publications of this type are the German *Chemisches Zentralblatt*,* and the Russian *Referativnyi Zhurnal*, *Khimiya*.

The only abstract journal concerned solely with the field of organometallic chemistry is *Organometallic Compounds* (D1), which covers patents and some of the chemical literature. About 5000 abstracts were published in 1969, relating to all aspects of Main Group and Transition element organometallic chemistry. Sections on olefin polymerization, polymerization catalysts, additives for plastics, paints, fuels, and lubricants, and related topics, follow a large section on organometallic chemistry.

D1. *Organometallic Compounds*, R. H. Chandler Ltd., London. Two volumes per year, published in monthly issues.

More recently, the explosion in volume of chemical publications, and the large increase in amounts of data which result, have led to the development of computer-based systems for processing, correlating, and retrieving the information. Many services of this type are available to the chemist, and they include various personalized services devoted to making rapid but useful literature surveys. Many obstacles remain to be overcome before systems will become available which will not produce a large amount of irrelevant information in addition to required items. One approach to the

* This publication ceased after volume 140 (1969), being replaced by *Chemischer Informationsdienst*, *Organische Chemie* and *Anorganische und physikalische Chemie*.

problem is based on a "profile" of interests, linked to certain keywords appearing in the titles of papers. However, the usefulness of these services depends upon the appearance of the keywords in the title, and although the use of additional keywords has been explored by at least one publisher, no general trends in contents-linked keywords are yet apparent.

Chemical Titles is a computer-produced list of titles of chemical papers arranged by keywords (KWIC, keyword in context), and produced by Chemical Abstracts Services. The titles appear so that the keywords are listed in the center of the column. It is based on the contents pages of some 700 journals abstracted in *Chemical Abstracts*, and appears twice monthly. For the most efficient use, a list of keywords is compiled, and the availability of this service on magnetic tape means that computer-based searches of these titles can be made.

The United Kingdom Chemical Information Service (UKCIS) uses these tapes to provide periodic searches against a profile.

The Institute of Scientific Information (ISI, Philadelphia, Pennsylvania) operates a computer-based weekly service called ASCA (Automatic Subject Citation Alert). Articles from prime scientific journals may be located through "cited item" terms as well as through title terms. Clusters of articles with common references will usually be about the same subject, so a reference used as a profile term will locate articles citing that reference, as articles are published. A similar principle is employed in the *Science Citation Index* for retrospective searching, where all items having a common reference are brought together beneath the item they cite.

Most of these aids to literature searching have been described recently in detail (4), and corresponding German developments in this area have also been discussed (5).

Many commercial "current awareness" services are available, and the most useful of these to the organometallic chemist is *Current Contents*. This consists of a weekly collection of photoreproduced contents pages of journals, together with a list of first author's addresses. The edition most likely to be consulted by the organometallic chemist is the *Physical and Chemical Sciences* section (originally separate *Physical Sciences* and *Chemical Sciences* editions).

E. Conference Reports

Many aspects of organometallic chemistry have been discussed at a variety of conferences held at various times and locations. Consequently,

important sources of information about the latest developments in the area are the reports and abstracts of such meetings.

Two of the most important series of meetings of this type are the International Conferences on Coordination Chemistry (ICCC) (E1), which began as a small meeting of chemists with a common interest at Welwyn in 1950, and the International Conferences on Organometallic Chemistry (ICOMC) (E2), of which the first was held in Cincinnati, Ohio, in 1963, under the title "Current Trends in Organometallic Chemistry." As these meetings grow in size and complexity, so do the numbers of communications presented at them, and abstracts of most of these are available. Often these conferences are sponsored by the International Union of Pure and Applied Chemistry, which then collects together and publishes the Main Lectures in its Journal *Pure and Applied Chemistry*. These are also available separately in bound volumes. The lectures provide useful summaries of the lecturer's contributions to a particular area, and these also have been listed in the Appendix.

- E1. International Conferences on Coordination Chemistry (ICCC). Information concerning these can be found in the following sources:
- 1.1 Welwyn, September 1950: This was an informal two-day meeting, and only a brief summary is available [*Nature (London)* **167**, 434 (1951)].
 - 1.2 Copenhagen, 1953: Proceedings published separately by the Danish Chemical Society, Copenhagen, 1954.
 - 1.3 Amsterdam, 1955: Abstracts of the main lectures, and the short papers, were published in *Rec. Trav. Chim.* **75**, No. 6 (1955).
 - 1.4 Rome, September 1957: The proceedings occupied *J. Inorg. Nucl. Chem.* **8** (1958), and were also issued separately.
 - 1.5 London, 1959: The main lectures, and abstracts of contributed papers, are contained in *Chem. Soc. Spec. Publ. No. 13* (1959).
 - 1.6 Detroit, 1961: The proceedings were published as S. Kirschner, ed., "Advances in the Chemistry of Coordination Compounds." Macmillan, New York (1961).
 - 1.7 Stockholm and Uppsala, 1962: Plenary lectures from this and most later conferences were published in *Pure Appl. Chem.*, and also as bound reprints. The lectures from the seventh conference comprise *Pure Appl. Chem.* **6**, 1–123 (1963).
 - 1.8 Vienna, 1964: The plenary lectures appeared in *Pure Appl. Chem.* **10**, 1–70 (1965). Books of abstracts of contributed papers were also issued for this and later conferences.
 - 1.9 St. Moritz, 1966: The main lectures of this conference, which was held in conjunction with the celebrations of the centenary of the birth of Alfred Werner, were published in *Helv. Chim. Acta, Fasc. Extraord. Alfred Werner* (Alfred Werner Commemoration Volume) in 1967.
 - 1.10 Tokyo and Nikko, 1967: The plenary lectures appeared in *Pure Appl. Chem.* **17**, 1–178 (1968).

- 1.11 Jerusalem and Haifa, 1968: The proceedings of this conference were published as M. Cais, ed., "Progress in Coordination Chemistry," Elsevier, Amsterdam (1968). The main lectures appeared in *Pure Appl. Chem.* **20**, 1-131 (1969).
- 1.12 Sydney, 1969: This conference was held in conjunction with the 22nd International Congress on Pure and Applied Chemistry. The main lectures appeared in *Pure Appl. Chem.* **24**, 289-441 (1970).
- 1.13 Cracow and Zakopane, 1970: The main lectures appeared in *Pure Appl. Chem.* **27**, 1-264 (1971).
- E2. International Conferences on Organometallic Chemistry (ICOMC). Not all proceedings of these conferences have been published.
 - 2.1 Cincinnati, Ohio, 1963: The first conference was held with the theme "Current Trends in Organometallic Chemistry," and the titles and authors of papers are listed in *J. Organometal. Chem.* **1**, 205-207 (1964).
 - 2.2 Madison, Wisconsin, 1965: Titles and authors of contributed papers are likewise listed in *J. Organometal. Chem.* **4**, 421-425 (1965).
 - 2.3 München, 1967: The plenary lectures appeared in *Pure Appl. Chem.* **17**, 179-272 (1968).
 - 2.4 Bristol, 1969: The abstracts of contributed papers are available as M. I. Bruce and F. G. A. Stone, eds., "Progress in Organometallic Chemistry," Bristol (1969), and the plenary and section lectures were published in *Pure Appl. Chem.* **23**, 375-503 (1970).

A series of conferences on different areas of inorganic chemistry, including organometallic chemistry, is sponsored by the journal *Inorganica Chimica Acta*, and these are held annually in Italy. Abstracts of contributed papers are published (E3). Lectures on various aspects of organo-transition metal chemistry have also been given at the Second International Symposium on Organosilicon Compounds (E4), and at the Ninth Robert E. Welch Foundation Conference on Chemical Research (E5).

- E3. *Inorganica Chimica Acta* Symposia, held in Venice. Long abstracts of contributed papers at these conferences have been issued. The subjects covered in these meetings were:
 - 3.1 1968: New aspects of the chemistry of metal carbonyls.
 - 3.2 1969: Advances in the chemistry of metal-carbon, metal-hydrogen, and metal-olefin complexes.
 - 3.3 1970: Reactivity and bonding in transition organometallic compounds.
- E4. Plenary lectures of the second International Symposium on Organosilicon Compounds, Bordeaux (1968) published in *Pure Appl. Chem.* **19**, 291-538 (1969).
- E5. Proceedings of the Ninth Robert A. Welch Foundation on Chemical Research, Houston, Texas (1965)—Organometallic Compounds. Not only the main lectures, but also the formal discussions, are fully reported in this volume. Of interest to organo-transition metal chemists are:
 - 5.1 G. Wilkinson: Transition metal-to-carbon bonds in aqueous solution and in catalysis, pp. 139-161.
 - 5.2 G. Wilke: Transition metals in organic chemistry, pp. 165-200 (9).
 - 5.3 F. A. Cotton: Structure and bonding in π -complexes, pp. 203-236.

- E6. Industrial Synthesis and Applications of Organometallics, eds. W. J. Considine and M. Tsutsui, New York Academy of Sciences, June 1964, published in *Ann. N.Y. Acad. Sci.* **125**, 1–248 (1965).

Other meetings which regularly contain papers on aspects of organo-metallic chemistry are those of the American Chemical Society. The abstracts of these meetings are usually worth perusing, papers generally appearing in the Inorganic and Organic sections. In 1970, the 159th and 160th meetings were held in Houston, Texas, and Chicago, Illinois. The proceedings of symposia held under the aegis of these general meetings are occasionally published later in the ACS *Advances in Chemistry Series*. The chemistry of organo-transition metal compounds have been surveyed in several of these (E7–9). The Faraday Society has also held an important meeting concerned with bonding in organometallic compounds, the proceedings of which have been issued as one of its Discussions series (E10).

- E7. ACS Advances in Chemistry Series No. 23 (1959): Metal-organic compounds. This book highlights various contemporary aspects of organo-metallic chemistry in many papers, including industrial applications.
- E8. ACS Advances in Chemistry Series No. 62 (1967): Werner Centennial Symposium.
- E9. ACS Advances in Chemistry Series No. 70 (1968): Homogeneous Catalysis. Proceedings of symposia at the 152nd ACS Meeting, New York, September 1966. Review papers in the above publications are listed in the Appendix.
- E10. Faraday Society Discussion No. 47 (1969): Bonding in metallo-organic compounds. This publication contains some 21 papers on various aspects of bonding in organo-metallic compounds, given at a meeting at Cambridge, March 1969.

F. Synthesis

The organometallic chemist often wishes to start his investigations with some quite sophisticated compound, which ideally should be available in high yield by a simple synthesis from readily available precursors. Detailed procedures for syntheses of this type are available in the series *Inorganic Syntheses*, *Organometallic Syntheses*, and to a lesser extent, *Organic Syntheses* (F1–3). These books contain tested syntheses of commonly used materials, and the first and last of these titles appear at frequent intervals.

Other sources, apart from the primary journals, include the German Brauer, now fortunately translated into English (F4), and many of the surveys of synthetic methods appearing in *Preparative Inorganic Reactions* (F5) have illustrative examples appended. Laboratory techniques peculiar to organometallic chemistry have also been described in books (e.g., F6–7), and in the series *Techniques of Inorganic Chemistry* (F8).

- F1. "Inorganic Syntheses." McGraw-Hill, New York. Vol. 1, ed. H. S. Booth (1939); vol. 2, ed. W. C. Fernelius (1946); vol. 3, ed. L. E. Audrieth (1950); vol. 4, ed. J. C. Bailar (1953); vol. 5, ed. T. Moeller (1957); vol. 6, ed. E. G. Rochow (1960); vol. 7, ed. J. Kleinberg (1963); vol. 8, ed. H. F. Holtzclaw (1966); vol. 9, ed. S. Y. Tyree (1967); vol. 10, ed. E. L. Muetterties (1967); vol. 11, ed. W. L. Jolly (1968); vol. 12, ed. R. W. Parry (1970).†
- F2. J. J. Eisch and R. B. King, eds., "Organometallic Syntheses." Academic Press, New York. Vol. 1, R. B. King, Transition metals (1965).
- F3. "Organic Syntheses." Wiley, New York. Annually, vols. 1–50 (1921–1970). Collective volumes 1 (2nd ed., 1958), 2 (1943), 3 (1955), 4 (1963). The latter assemble and revise the syntheses contained in the annual volumes for each decade.
- F4. G. Brauer, "Handbuch der Präparativen Anorganischen Chemie." Enke, Stuttgart, Vol. 1 (1960), vol. 2 (1962). English translation: "Preparative Inorganic Chemistry." Academic Press, New York. Vol. 1 (1963), vol. 2 (1965).
- F5. W. L. Jolly, ed., "Preparative Inorganic Reactions." Wiley, New York. Vol. 1 (1964), vol. 2 (1965), vol. 6 (1966), vol. 7 (1968), vol. 5 (1968).
- F6. W. L. Jolly, "Synthetic Inorganic Chemistry." Prentice-Hall, Englewood Cliffs, New Jersey, 1960.
- F7. R. J. Angelici, "Synthesis and Technique in Inorganic Chemistry." Saunders, Philadelphia, 1969. Designed for undergraduate laboratory courses in inorganic chemistry.
- F8. H. B. Jonassen and A. Weissberger, "Techniques of Inorganic Chemistry." Wiley (Interscience), New York. Vol. 1 (1963), vol. 2 (1963), vol. 3 (1963), vol. 4 (1965), vol. 5 (1965), vol. 6 (1966), vol. 7 (1968). This series is not yet generally useful to organometallic chemists, with the exception of the article:
 8.1 S. Herzog, J. Dehnert, and K. Lühder: An expedient method for preparative procedures in an inert atmosphere, vol. 7, pp. 119–149 (26).
 Future volumes will be issued in the series "Physical Methods in Chemistry," ed. A. Weissberger and B. W. Rossiter. Wiley, New York.

Several journals in which the emphasis is largely on synthesis have appeared during the last two or three years. There are several useful reviews and methods in *Synthesis* (F9) which appertain to organometallic chemistry, and two even more closely related publications are *Organometallics in Chemical Synthesis* (F10), from the same publishers as the *Journal of Organometallic Chemistry*, and *Synthesis in Inorganic and Metalorganic Chemistry* (F11). The latter is another rapid communications journal, reproducing the authors' typewcripts, and aims to collect syntheses of new compounds, new procedures for the syntheses of known compounds, and new experimental methods and techniques. Some organometallic syntheses have also been reported in *Organic Preparations and Procedures* (F12).

- F9. *Synthesis*, an international journal of methods in synthetic organic chemistry, G. Thieme, Stuttgart: Academic Press, New York. 1969 ff. Published monthly since September 1969.

- F10. *Organometallics in Chemical Synthesis*, Elsevier, Amsterdam. Vols. 1 ff. (1970 ff; one volume per year).
- F11. *Synthesis in Inorganic and Metalorganic Chemistry*, Dekker, New York. Vols. 1 ff (1971 ff).
- F12. *Organic Preparations and Procedures*, Dekker, New York. Vols. 1 ff (1969 ff; one volume per year).

G. Compound and Formula Registers

It is often convenient to have quick access to the properties of organometallic compounds, especially when these occur as byproducts from reactions designed to give complexes of a different type. A noncritical compendium of organo-transition metal compounds, reported between 1937 and 1964, is volume 1 of Dub's "Organometallic Compounds" (G1). This useful work is currently being extended to 1968 coverage. Other, less detailed, handbooks of organometallic chemistry are available (G2-3), but do not have the detail of Dub's work. Organometallic chemistry does not yet have its Gmelin* or Beilstein, nor is it likely that any single author or small group would have the ability (or even stamina!) to collect together all the information that is currently available and published. However, much organometallic chemistry is now being included in the later editions and supplements of Gmelin.

- G1. M. Dub, ed., "Organometallic Compounds," 2nd ed. Springer, Berlin, 1966. Vol. 1, Compounds of the transition metals. Surveys the literature 1937-1964. A separate volume contains a formula index, and a supplement covering the literature 1965-1968 is in preparation.
- G2. H. C. Kaufman, "Handbook of Organometallic Compounds," Van Nostrand, New York, 1961. Compilation of data on several thousand compounds, but does not include many transition metal compounds, noncritical and occasionally lists compounds such as Mn_2O_7 .
- G3. N. Hagihara, M. Kumada, and R. Okawara, "Handbook of Organometallic Compounds," Benjamin, New York, 1968. Sections dealing with transition metal compounds on pp. 766-776 and 822-931. This book is an English translation of a Japanese publication, issued by Asakura, Tokyo, and is a noncritical list of compounds.

All compounds indexed in *Chemical Abstracts* since 1965 (vol. 62) have been allotted a Registry Number, based on an algorithm for generating a machine-language representation of the two-dimensional and stereochemical arrangements of atoms and groups of chemical compounds. The

* Note added in proof. This statement is no longer correct. The Gmelin-Institut has commenced publication of volumes in the 8th edition of "Gmelin's Handbuch der anorganische Chemie" specifically concerned with organometallic compounds. The first volume describes the derivatives of vanadium and chromium.

Registry Number, which is unique to each compound, is used to link the structure with names, references, and other information within the Chemical Abstracts Service Registry Number System. However, there is no way to generate a Registry Number from a given structure, and data on specific compounds can only be recovered by finding the Registry Number first. The first formula index to use these numbers will be that for vol. 71 (1969).

Index Chemicus (G4) is a more comprehensive and accessible index of new compounds for which analytical data and molecular formulas are available. The publication summarizes this type of information from over 200 key journals, usually within 45 days of the original publication date. Several other instrumental data are usually given, in addition to an abstract of the paper. Some indication of the scope is given by the cumulative index for 1960–1967, which listed some 850,000 new compounds. In 1968 alone, about 165,000 new compounds were described.

Access to all this information is provided by the *Index Chemicus Registry System* (ICRS), which contains records of new compounds and associated data on magnetic tape (6). Structures are described by the Wiswesser Line Notation (7), a system for describing chemical formulas in terms of a linear groups of symbols. A recent development is the *ICRS Substructure Index* (G5), which enables manual searches to be made for new chemical information, and is based on the occurrence of fragments of structures, the most common of which are illustrated as conventional structural diagrams.

- G4. Current Abstracts of Chemistry and Index Chemicus, published by Institute for Scientific Information, Philadelphia, Pennsylvania. Other publications of ISI include the ASCA system; the Science Citation Index; and Current Contents.
- G5. ICRS Substructure Index, an alphabetical listing in Wiswesser Line Notation of each new compound reported in G4 above. See also a fuller description in *J. Chem. Doc.* **10**, 54 (1970).

REFERENCES

- 1. Bottle, R. T., ed., "The Use of Chemical Literature," 2nd ed. Butterworth, London, 1969.
- 2. Cahn, R. S. "Survey of Chemical Publications," p. 8. The Chemical Society, London, 1965.
- 3. Garfield, E. *Nature, (London)* **227**, 669 (1970). This article resulted in several letters which were published in later issues of the journal.
- 4. UKCIS—The United Kingdom Chemical Information Service: Batten, W., *Chem. Brit.* **6**, 420 (1970); Citations in Chemistry (SIC): Cawell, A. E., *Chem. Brit.* **6**, 414 (1970). Other relevant articles in this issue include: Hyams, M., Chemical patents information, p. 416; and Polton, D. J., IUPAC notation in chemical substructure searching, p. 430.

5. Chemical Information Services, *Angew. Chem.* **82**, 563–633 (1970); *Angew. Chem. Int. Ed., Engl.* **9**, 545–610 (1970). The articles collected in this issue cover: Present day communication in chemistry—problems and possibilities (G. Kresze); Chemical information services (C. Weiske); Theoretical aspects of communication in chemistry (R. Fugmann); Use of the IDC (International Dokumentationsgesellschaft für Chemie mbH) system (M. A. Lobeck); Versatile computer techniques for searching by structural formulas, partial structures, and classes of compounds (E. Meyer); TOSAR—a topological method for the representation of synthetic and analytical relations of concepts (R. Fugmann and others); "Dokumentationsring der chemisch-pharmazeutischen Industrie"—Aims and methods (W. Nübling and W. Steidle); A system for the documentation of chemical reactions (O. Schier and others); CCBF—A system for computer processing of chemical and biological facts (G. Ohnacker and W. Kalbfleisch).
6. Garfield, E., Revesz, G. S., Granito, C. E., Dorr, H. A., Calderon, M. M., and Warner A., *J. Chem. Doc.* **10**, 54 (1970).
7. Smith, E. G., "The Wiswesser Line-Formula Chemical Notation," McGraw-Hill, New York, 1968; see also Palmer G., *Chem. Brit.* **6**, 422 (1970); Campey, L. H., Hyde, E., and Jackson, A. R. H., *Chem. Brit.* **6**, 427 (1970).

APPENDIX *

This table has been compiled from articles which have come to the author's attention either directly or from other references. There is made no claim for completeness, and this is particularly true for articles published in languages other than English. However, it is believed that the large majority of important reviews and surveys have been included. With the exception of a few articles on metal carbonyls and olefin complexes, these articles have appeared since 1950. Nearly 500 articles are listed. In the expectation of a later updating of this list, the author would appreciate any missing items being brought to his notice.

The references are broadly classified according to the subject(s) reviewed, which have been arbitrarily ordered as follows:

1. Historical and biographical
3. Reviews, of organometallic chemistry, of a general nature
3. General experimental techniques
4. Organo-element chemistry, i.e. reviews wherein the general organometallic chemistry of a specific element or group of elements is described
5. Metal carbonyls
6. Metal carbonyls and olefin complexes (prior to 1950)
7. Metal carbonyl anions
8. Metal carbonyl cations
9. Metal carbonyl hydrides and halides
10. Compounds containing bonds between Transition Metals and Main Group metals or metalloids
11. Metal-metal bonded and cluster compounds of Transition Metals
12. Lewis Base complexes—general
13. Lewis Base complexes—ligands with Group V donor atoms
14. Lewis Base complexes—ligands with Group VI donor atoms
15. Metal-carbon σ bonds

*The Author Index for this Appendix appears on pp. 445–450.

16. Fluorocarbon complexes
17. Complexes containing other halocarbons, or cyanocarbons
18. Hydrocarbon-metal π -complexes—general
19. Olefin and acetylene complexes
20. Allyl complexes
21. Cyclobutadiene complexes
22. Cyclopentadienyl and arene complexes
23. Complexes containing larger ring systems
24. Fluxional organometallic molecules
25. Metallocene chemistry, i.e. organic chemistry of ferrocene and related molecules
26. Metallocarborane complexes
27. Kinetics and mechanisms of reactions
28. Organic syntheses via organometallics
29. Catalysis by organometallics
30. Organometallic polymerization catalysts
31. Oxidative addition and related reactions
32. Ligand reactivity
33. Photochemistry
34. Complexes of biological interest
35. Electronic structures of organometallic compounds
36. Physical methods—infrared spectroscopy
37. Physical methods—nuclear magnetic resonance
38. Physical methods—mass spectrometry
39. Miscellaneous physical methods
40. Structural studies
41. Energetics—bond energies and thermodynamic properties
42. Molecular nitrogen (dinitrogen) complexes
43. Other topics related to organometallic chemistry

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
<i>1. Historical and biographical</i>					
1.1	R. K. Freidlina, M. I. Kabachnik, and V. V. Korshak	<i>Usp. Khim.</i> 38 , 1539 (1969); <i>Russ. Chem. Rev.</i> 38 , 684 (1969)	New contributions to the develop- of organoelementary and organic chemistry	15 (164)	A. N. Nesmeyanov 70th birthday: summary of work on ferrocene, arene compounds, metal car- bonyls, metal-metal bonds, Group IV organometallic compounds
1.2	H. Gilman	<i>Advan. Organometal. Chem.</i> 7 , 1 (1968)	Some personal notes on more than one-half century of organo- metallic chemistry	52 (46)	
1.3	F. Hein	<i>Z. Chem.</i> 1 , 105 (1961)	Of Nature, and the new develop- ments in chemistry	15 (91)	
1.4	W. Hieber	<i>Advan. Organometal. Chem.</i> 8 , 1 (1970)	Metal carbonyls, forty years of research	28 (111)	
1.5	A. N. Nesmeyanov	<i>Usp. Khim.</i> 28 , 1164 (1959)	D. I. Mendeleev's periodic system of the elements and organic chemistry	37 (412)	Russ. Position of organometallic compounds in chemistry
1.6	W. P. Neumann	<i>Naturwissenschaften</i> 15 , 553 (1968)	The increasing significance of organometallic chemistry	5 (26)	Historical review
1.7	O. Y. Okhlobystin	<i>Zh. Obshch. Khim.</i> 37 , 2376 (1967)	Development of organometallic chemistry in the Soviet Union	17 (179)	
1.8	O. Y. Okhlobystin	<i>Priroda (Moscow)</i> No. 9 , 40 (1969)	Elements of the periodic system and organic chemistry	5	A. N. Nesmeyanov 70th birthday: review of his work concerning organometallic compounds
1.9	S. Pasynkiewicz	<i>Wiad. Chem.</i> 23 , 167 (1969)	Development of organometallic chemistry	16 (14)	Polish
1.10	M. D. Rausch	<i>Advan. Chem. Ser.</i> 62 , 486 (1966)	The history and development of organo-transition metal chem- istry	46 (268)	

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
<i>1. Historical and biographical (cont'd)</i>					
1.11	E. G. Rochow	<i>Abstr. 17th Int. Congr. Pure Appl. Chem.</i> 1, 136 (1959)	From structure to synthesis of organometallic compounds	9 (10)	
1.12	E. G. Rochow	<i>Advan. Organometal. Chem.</i> 9, 1 (1970)	Of time and carbon-metal bonds	19 (28)	
1.13	V. I. Spitsyn and E. G. Perevalova	<i>Zh. Obshch. Khim.</i> 40, 505 (1970)	Research of A. N. Nesmeyanov on organo-iron compounds	10 (101)	70th birthday review
1.14	F. G. A. Stone	<i>Pure Appl. Chem.</i> 10, 37 (1965)	The role of organometallic compounds in the development of coordination chemistry	15 (61)	Plenary lecture, 8ICCC
1.15	N. A. Vol'kenau, B. L. Dyatkin, S. T. Ioffe, V. I. Kuznetsov, L. G. Makarova, O. Y. Okhlobystin, and R. A. Sokolik	<i>Razv. Org. Khim. SSSR, 1917-1967, Akad. Nauk SSSR, Inst. Istor. Estestvoza Tekh.</i> 100 (1967)	Chemistry of heteroorganic compounds	85 (957)	Survey of the development of organometallic chemistry in the USSR, written for 50 years of USSR
1.16	K. Ziegler	<i>Advan. Organometal. Chem.</i> 6, 1 (1968)	A forty years' stroll through the realms of organometallic chemistry	17 (51)	
<i>2. Reviews of a general nature</i>					
2.1	D. C. Bradley	<i>Record Chem. Progr.</i> 21, 179 (1960)	Organo-compounds of transition metals	10 (20)	
2.2	J. J. Eisch and H. Gilman	<i>Advan. Inorg. Chem. Radiochem.</i> 2, 61 (1960)	Organometallic compounds	43 (145)	Only 2 pp. on transition metal organometallics!
2.3	G. A. Gamlen	<i>Mod. Chem. Ind., Proc. IUPAC Symp.</i> 239 (1968)	Coalescence of modern inorganic and organic chemistry	5	Organometallics and homogeneous catalysis

2.4	G. A. Gamlen	<i>Disc. Faraday Soc.</i> No. 47, 7 (1969)	From ferrocene to uranocene	13 (51)	General survey, opening a symposium on bonding in organometallics (see E10)
2.5	N. Hagihara	<i>Yukagaku</i> 14, 462 (1965)	The chemistry of organometallic complexes	8 (41)	Japan.
2.6	K. Harasawa	<i>Kagaku Kogyo</i> 18, 908 (1967)	Advances in organometallic chemistry	9 (63)	Japan. Metallocenes, cyclobutadiene and carbonyl compounds, fluoro complexes
2.7	F. Hein	<i>Angew. Chem. Ausg.</i> A 62, 205 (1950)	Complex compounds in inorganic chemistry	8	P. Pfeiffer's 75th birthday. Carbonyls, nitrosyls and organometallics
2.8	E. Hoggarth	<i>Advan. Sci.</i> 23, 652 (1967)	Organometallic chemistry and its growing significance in industry	6 (13)	
2.9	H. D. Kaesz	<i>J. Chem. Educ.</i> 40, 159 (1963)	Organometallic derivatives of the transition elements	10 (58)	
2.10	M. Kumada	<i>Yuki Gosei Kagaku</i> <i>Kyoki Shi</i> 20, 177 (1962)	Chemistry of organometallic compounds	13 (127)	Japan.
2.11	M. F. Lappert	<i>Chem. Brit.</i> 5, 342 (1969)	Organometallic chemistry	5 (46)	
2.12	R. R. Myers	<i>J. Paint Technol.</i> 39, 565 (1967)	π -Bonded structures	4	Opening remarks at symposium. See also 25.23, 25.27
2.13	M. Nakahara	<i>Bussei</i> 10, 198 (1969)	Metal compounds of unfamiliar oxidation states	8 (14)	Japan. Includes carbonyls, Vaska's complex
2.14	M. Nilsson	<i>Sv. Kem. Tidskr.</i> 80, 192 (1968)	Metalorganic chemistry	6 (35)	Swed. Organo-nickel and -copper compounds and catalysts
2.15	E. G. Nottes and J. F. Cordes	<i>Erdoel Kohle, Erdgas,</i> <i>Petrochem.</i> 18, 885 (1965)	Studies on organometallic anti-knock agents	9 (25)	
2.16	S. Otsuka	<i>Kagaku Kogyo</i> 21, 464 (1970)	Recent topics in the chemistry of complexes	9 (91)	Japan. Metal-metal bonds, nitrogen fixation, carbenes, etc.

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
2. <i>Reviews of a general nature (cont'd)</i>					
2.17	A. K. Prokof'ev, V. I. Bregadze, and O. Y. Okhlobystin	<i>Usp. Khim.</i> 39 , 412 (1970); <i>Russ. Chem. Rev.</i> 39 , 196 (1970)	Intramolecular coordination in organic derivatives of the elements	17 (210)	Mostly main group examples
2.18	F. G. A. Stone	<i>Rev. Pure Appl. Chem.</i> 17 , 41 (1967)	Some organometallic syntheses	8 (62)	
2.19	W. Wardlaw and D. C. Bradley	<i>Endeavour</i> 14 , 140 (1955)	Organic compounds of the metals	6 (19)	
2.20	H. Werner	<i>Chem. Unserer Zeit</i> 3 , 152 (1969)	Organometallic complex chemistry. Central field of chemical research	7 (0)	
2.21	T. P. Whaley and A. P. Giraitis	<i>Chem. Eng. Prog.</i> 58 , (8), 65 (1962)	Organometallics as vehicles for metals	3 (0)	
3. <i>General techniques</i>					
3.1	S. Herzog and J. Dehnert	<i>Z. Chem.</i> 4 , 1 (1964)	A rational method for working in the absence of air	11 (14)	Few transition-metal organometallics
3.2	R. G. Jones and H. Gilman	<i>Chem. Rev.</i> 54 , 835 (1954)	Methods of preparation of organometallic compounds	56 (471)	
3.3	V. D. Nefedov, M. A. Toropova, and E. N. Sinotova	<i>Usp. Khim.</i> 38 , 1913 (1969); <i>Russ. Chem. Rev.</i> 38 , 873 (1969)	Radiochemical methods for preparing organometal (metalloid) compounds	11 (147)	
3.4	K. Sonagashira and N. Hagihara	<i>Kogyo Kagaku Zasshi</i> 73 , 40 (1970)	Formation of organometallic complexes by reaction between organic compounds and metals	6 (23)	

See also A41.1

4. Organo-element chemistry

- | | | | | | |
|------|--|---|--|-------------|---|
| 4.1 | H. Gysling and
M. Tsutsui | <i>Advan. Organometal.
Chem.</i> 9 , 361 (1970) | Organolanthanides and organo-
actinides | 35
(135) | |
| 4.2 | R. S. P. Coutts and
P. C. Wailes | <i>Advan. Organometal.
Chem.</i> 9 , 135 (1970) | Organic complexes of lower-valent
titanium | 59
(192) | |
| 4.3 | T. Ishino and
S. Minami | <i>Kagaku No Ryoiki</i>
11 , 657 (1957) | Organic compounds of titanium | 12
(142) | Japan. |
| 4.4 | G. A. Razuvaev and
V. N. Latyaeva | <i>Organometal Chem.
Rev.</i> 2 , 349 (1967) | Covalent organic compounds of
titanium | 33
(117) | |
| 4.5 | I. Shihara | <i>Yuku Gosei Kagaku
Kyokai Shi</i> 28 , 793
(1970) | Organic titanium compounds and
advances in their organic synthe-
sis | 14
(50) | Japan. |
| 4.6 | I. Shihara,
W. T. Schwartz,
and H. W. Post | <i>Chem. Rev.</i> 61 , 1
(1961); <i>Usp. Khim.</i>
34 , 44 (1965) | The organic chemistry of titanium | 30
(423) | |
| 4.7 | A. L. Suvorov and
S. S. Spasski | <i>Usp. Khim.</i> 28 , 1267
(1959) | Organic compounds of titanium | 43
(274) | Russ. |
| 4.8 | A. Watanabe | <i>Yuki Gosei Kagaku
Kyokai Shi</i> 18 , 88
(1960) | Organotitanium compounds | 9
(111) | Japan. |
| 4.9 | D. Nicholls | <i>Coord. Chem. Rev.</i> 1 ,
379 (1966) | The coordination chemistry of
vanadium | 36
(168) | |
| 4.10 | H. H. Zeiss and
R. P. A. Sneeden | <i>Angew. Chem.</i> 77 ,
401 (1965); <i>Angew.
Chem. Int. Ed.</i>
<i>Engl.</i> 6 , 435 (1967) | Sigma-bonded organochromium
compounds. Hydrogen transfer
reactions | 8
(40) | English version is revised version
of German edition |
| 4.11 | L. Jacque and
G. Kersaint | <i>Chim. Ind., Genie
Chim.</i> 100 , 429,
777 (1968) | Organic complexes of molybdenum | 47
(362) | |
| 4.12 | P. C. H. Mitchell | <i>Coord. Chem. Rev.</i>
1 , 315 (1966) | Coordination compounds of molyb-
bdenum | 36
(180) | |
| 4.13 | G. Spengler and
J. Gansheimer | <i>Angew. Chem.</i> 69 ,
523 (1957) | Organic complexes of molybdenum | 7
(61) | |

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
4. <i>Organo-element chemistry (cont'd)</i>					
4.14	K. N. Anisimov, A. A. Ioganson, and N. E. Kolobova	<i>Usp. Khim.</i> 37 , 380 (1968); <i>Russ. Chem. Rev.</i> 37 , 184 (1968)	The chemistry of manganese carbonyl	14 (229)	
4.15	K. V. Kotegov, O. N. Pavlov, and V. P. Shvedov	<i>Advan. Inorg. Chem. Radiochem.</i> 11 , 1 (1968)	Technetium	90 (273)	
4.16	K. Schwochau	<i>Angew. Chem.</i> 76 , 9 (1964)	Chemistry of technetium	11 (157)	
4.17	J. E. Fergusson	<i>Coord. Chem. Rev.</i> 1 , 459 (1966)	Recent advances in the coordination chemistry of rhenium	45 (287)	
4.18	N. Hagihara	<i>Kagaku (Kyoto)</i> 17 , 1010 (1962)	Organic iron compounds	9 (38)	Japan.
4.19	M. Hidai	<i>Yuki Gosei Kagaku Kyokai Shi</i> 27 , 1117 (1969)	Diiron enneacarbonyl	3 (6)	Japan.
4.20	M. I. Bruce and F. G. A. Stone	<i>Angew. Chem.</i> 80 , 460 (1968); <i>Angew. Chem. Int. Ed. Engl.</i> 7 , 427 (1968)	Dodecacarbonyltriruthenium	6 (74)	
4.21	M. Hidai	<i>Yuki Gosei Kagaku Kyokai Shi</i> 27 , 1243 (1969)	Triruthenium dodecacarbonyl	3 (13)	Japan.
4.22	W. P. Griffith	<i>Quart. Rev.</i> 19 , 254 (1965)	Osmium and its compounds	20 (111)	Known organometallic chemistry, pp. 268-272
4.23	A. J. Chalk and J. F. Harrod	<i>Advan. Organometal. Chem.</i> 6 , 119 (1968)	Catalysis by cobalt carbonyls	52 (161)	
4.24	R. F. Heck	<i>Advan. Organometal. Chem.</i> 4 , 243 (1966)	Synthesis and reactions of alkylcobalt and acylcobalt tetracarbonyls	24 (30)	

4.25	M. Hidai	<i>Yuki Gosei Kagaku Kyokai Shi</i> 27 , 1018 (1969)	Chlorotris(triphenylphosphine)-rhodium(I)	4 (17)	Japan. Summary of catalytic reactions
4.26	K. A. Taylor	<i>Advan. Chem. Ser.</i> 70 , 195 (1968)	Chelate complexes of iridium—their chemistry and use in catalysis	12 (52)	
4.27	G. N. Schrauzer	<i>Advan. Organometal. Chem.</i> 2 , 1 (1964)	Some advances in the organometallic chemistry of nickel	48 (107)	
4.28	G. Wilke	<i>Pure Appl. Chem.</i> 17 , 179 (1968)	Organonickel compounds	16 (25)	Plenary lecture, 3ICOMC
4.29	J. R. Miller	<i>Advan. Inorg. Chem. Radiochem.</i> 4 , 133 (1962)	Recent advances in the stereochemistry of nickel, palladium and platinum	63 (270)	
4.30	R. J. Cross	<i>Organometal. Chem. Rev.</i> , 2 , 97 (1967)	σ -Complexes of platinum(II) with hydrogen, carbon and other elements of Group IV	44 (81)	
4.31	F. R. Hartley	<i>Organometal. Chem. Rev. Sect. A</i> 6 , 119 (1970)	Starting materials for the preparation of organometallic complexes of platinum and palladium	19 (77)	
4.32	R. Hüttel	<i>Brennst.-Chem.</i> 50 , 281, 331 (1969)	Palladium salts and palladium complexes in organic chemistry	5 + 4 (123)	
4.33	R. Hüttel	<i>Synthesis</i> 225 (1970)	Palladium salts and palladium complexes in preparative organic chemistry	31 (162)	
4.34	J. S. Thayer	<i>Organometal. Chem. Rev., Sect. A</i> 5 , 53 (1970)	Organoplatinum(IV) compounds	14 (71)	
4.35	G. Wilkinson	<i>Platinum Metals Rev.</i> 8 , 16 (1964)	Organometallic compounds of the platinum metals	7 (5)	
4.36	C. D. M. Beverwijk, G. J. M. van der Kerck, A. J. Leusink, and J. G. Noltes	<i>Organometal. Chem. Rev., Sect. A</i> 5 , 215 (1970)	Organosilver chemistry	66 (240)	

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
4. <i>Organo-element chemistry (cont'd)</i>					
4.37	B. Armer and H. Schmidbaur	<i>Angew. Chem.</i> 82 , 120 (1970); <i>Angew.</i> <i>Chem. Int. Ed.</i> <i>Engl.</i> 9 , 101 (1970)	Organogold chemistry	13 (94)	
4.38	J. Chatt	<i>Chem. Rev.</i> 47 , 7 (1951)	The addition compounds of olefins with mercuric salts	37 (73)	
	See also: A27(V); A28(Ti); A29 (Cu, Ag, Au)				
5. <i>Metal carbonyls</i>					
5.1	E. W. Abel	<i>Quart. Rev.</i> 17 , 133 (1963); <i>Usp. Khim.</i> 34 , 1127 (1965)	The metal carbonyls	27 (144)	
5.2	E. W. Abel and F. G. A. Stone	<i>Quart. Rev.</i> 23 , 325 (1969)	The chemistry of transition metal carbonyls: structural considera- tions	47 (209)	The best up-to-date survey of this important topic. Many references enable material to be followed up in detail
5.3	E. W. Abel and F. G. A. Stone	<i>Quart. Rev.</i> 24 , 498 (1970)	The chemistry of transition metal carbonyls: synthesis and reac- tivity	55 (360)	
5.4	M. Bigorgne and J. Bénard	<i>Rev. Chim. Miner.</i> 3 , 831 (1966)	Some aspects of the chemistry of metal carbonyls	29 (61)	
5.5	W. Hieber, W. Beck, and G. Zeitler	<i>Angew. Chem.</i> 73 , 364 (1961)	New observations on reactions of metal carbonyls, especially man- ganese carbonyl	5 (17)	
5.6	J. C. Hileman	<i>Prep. Inorg. React.</i> 1 , 77 (1964)	Metal carbonyls	44 (140)	Many syntheses now superseded by new low-pressure reactions
5.7	J. Jaluvka and L. Smik	<i>Chem. Listy</i> 62 , 1094 (1968)	Metal carbonyls	17 (154)	Czech.
5.8	L. Malatesta	<i>Chim. Ind. (Milan)</i> 46 , 894 (1964)	Carbonyl compounds of transition metals	8	

5.9	H. Ohm	<i>Chem. Weekbl.</i> 55 , 93 (1959)	Metal carbonyls	9 (53)	Dutch
5.10	A. Paris	<i>Ind. Chim.</i> 38 , 125 (1951)	The metal carbonyls: preparation, structure, uses	7 (11)	
5.11	H. Podall	<i>J. Chem. Educ.</i> 38 187 (1961)	Recent developments in metal carbonyl synthesis	5 (40)	
5.12	M. E. Strem	<i>Ann. N.Y. Acad. Sci.</i> 145 , 123 (1967)	Metal carbonyls: their synthesis and utility	18 (70)	
See also: A21; A37.2; A38.10; A39.1; 1.4; 28.15; 28.20					
6. <i>Metal carbonyls and olefin complexes (published before 1950)</i>					
6.1	J. S. Anderson	<i>Quart. Rev.</i> 1 , 331 (1947)	Chemistry of the metal carbonyls	27 (98)	
6.2	A. A. Blanchard	<i>Chem. Rev.</i> 21 , 3 (1937)	The volatile metal carbonyls	36 (92)	
6.3	A. A. Blanchard	<i>Chem. Rev.</i> 26 , 409 (1940)	Valence relations among the metal carbonyls	14 (64)	
6.4	A. A. Blanchard	<i>Science</i> 94 , 311 (1941)	Metal carbonyls	7	Edgar Fahs Smith memorial lecture
6.5	W. Hieber	<i>Z. Elektrochem.</i> 43 , 390 (1937)	On metallic carbonyls	8	
6.6	W. Hieber	<i>Die Chemie</i> 55 , 7, 24 (1942)	The present status of the chemistry of metal carbonyls	5 + 5	
6.7	W. Hieber	<i>FIAT Rev. German Sci.</i> , 1939–1946. <i>Inorg. Chem.</i> Pt. II, 108 (1948)	Metal carbonyls	38 (76)	Account of German research during WWII
6.8	M. Lehne	<i>Rev. Sci.</i> 84 , 295 (1946)	The metallic carbonyls	8	
6.9	A. Mittasch	<i>Kolloid-Z.</i> 104 , 139 (1943)	The story of the metal carbonyls	3 (9)	
6.10	R. L. Mond	<i>Chim. Ind. (Paris)</i> 21 , 681, 937 (1929)	Metallic carbonyls	20 + 4 (160)	

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
<i>6. Metal carbonyls and olefin complexes (published before 1950) (cont'd)</i>					
6.11	R. L. Mond	<i>J. Soc. Chem. Ind.</i> 49 , 271T, 283T, 287T (1930)	The metal carbonyls	8 + 2 + 4	See ref. 6.10
6.12	P. G. Spacu	<i>Rev. Stiint. "V. Adamachi"</i> 29 , 116 (1943)	The metal carbonyls and their significance in chemistry and in industry	22	Rom.
6.13	W. E. Trout	<i>J. Chem. Educ.</i> 14 , 453, 575 (1937); 15 , 77, 113 (1938)	The metal carbonyls. I History. II Preparation. III Constitution. IV Properties. V Physiological properties. VI Derivatives. VII Industrial significance	10 + 7 + 7 + 9 (114)	
6.14	N. Wardlaw	<i>Annu. Rep. Progr. Chem.</i> 31 , 99 (1934)	Metallic carbonyl and nitrosyl compounds	10 (36)	
6.15	A. J. E. Welch	<i>Annu. Rep. Progr. Chem.</i> 38 , 71 (1941)	Metallic carbonyls and nitrosyls	13 (57)	
6.16	F. Hein	<i>Angew. Chem.</i> 51 , 503 (1938)	New developments in the field of metalorganic compounds	16 (41)	
6.17	R. N. Keller	<i>Chem. Rev.</i> 28 , 229 (1941)	Coordination compounds of olefins with metallic salts	39 (130)	
See also: A11.					
<i>7. Metal carbonyl anions</i>					
7.1	M. I. Bruce and F. G. A. Stone	<i>Angew. Chem.</i> 80 , 835 (1968); <i>Angew. Chem. Int. Ed. Engl.</i> 7 , 747 (1968)	Nucleophilic reactions of metal carbonyl anions with fluoro-carbons	7 (38)	
7.2	W. Hieber, W. Beck, and G. Braun	<i>Angew. Chem.</i> 72 , 795 (1960)	Anionic carbonyl complexes	7 (84)	

7.3	R. B. King	<i>Advan. Organometal. Chem.</i> 2 , 157 (1964)	Reactions of alkali metal derivatives of metal carbonyls and related compounds	100 (251)	
8. <i>Metal carbonyl cations</i>					
8.1	E. W. Abel and S. P. Tyfield	<i>Advan. Organometal. Chem.</i> 8 , 117 (1970)	Metal carbonyl cations	51 (247)	
8.2	M. H. B. Stiddard	<i>Rev. Chim. Miner.</i> 3 , 801 (1966)	Carbonyl complexes of transition metals in positive oxidation states	13 (123)	
See also: A58.1					
9. <i>Metal carbonyl hydrides and halides</i>					
9.1	J. Chatt	<i>Science</i> 160 , 723 (1968)	Hydride complexes	7 (27)	Of transition metals
9.2	J. Chatt and B. L. Shaw	<i>Abstr. 17th Int. Congr. Pure Appl. Chem.</i> 1 , 147 (1959)	Hydrides and complex hydrides of the transition metals	20 (50)	
9.3	A. P. Ginsberg	<i>Transition Metal Chem.</i> 1 , 111 (1965)	Hydride complexes of the transition metals	127 (331)	
9.4	M. L. H. Green	<i>Angew. Chem.</i> 72 , 719 (1960)	Hydride complexes of the transition metals	7 (94)	
9.5	M. L. H. Green	<i>Endeavour</i> 26 , 129 (1967)	Hydride complexes of transition metals	5 (10)	
9.6	M. L. H. Green and D. J. Jones	<i>Advan. Inorg. Chem. Radiochem.</i> 7 , 115 (1965)	Hydride complexes of the transition metals	68 (273)	
9.7	J. Lewis	<i>Sci. Progr.</i> 49 , 67 (1961)	Recent advances in science: inorganic chemistry	11 (37)	Hydrides mainly; also CO and cyclopentadienyl complexes
9.8	B. Stalinski	<i>Fizykochem. Ciala Stalego</i> 185 (1967)	Structure and properties of the transition metal hydrides	33 (196)	Polish
9.9	M. W. Anker, R. Colton, and I. B. Tomkins	<i>Rev. Pure Appl. Chem.</i> 18 , 23 (1968)	Substituted halocarbonyls of the Group VI transition metals	18 (77)	

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
10. Complexes containing bonds between Transition Metals and Main Group Metals (metalloids)					
10.1	W. Jehn	<i>Z. Chem.</i> 9 , 170 (1969)	Organometallic metal carbonyls	8 (128)	
10.2	N. E. Kolobova, A. B. Antonova, and K. N. Anisimov	<i>Usp. Khim.</i> 38 , 1802 (1969); <i>Russ. Chem. Rev.</i> 38 , 822 (1969)	Derivatives of metal carbonyls containing a bond between atoms of transition metals and Group IVB elements	18 (176)	
10.3	A. G. MacDiarmid, Y. L. Baay, J. F. Bald, A. D. Berry, S. K. Gondal, A. P. Hagen, M. A. Nasta, F. E. Saalfeld, and M. V. McDowell	<i>Pure Appl. Chem.</i> 19 , 431 (1969)	Properties of silicon derivatives of cobalt, manganese and iron carbonyls	18 (73)	Lecture, 2nd Int. Symp. Organosilicon Chem., Bordeaux, 1968
10.4	H. Nöth and G. Schmid	<i>Allg. Prakt. Chem.</i> 17 , 610 (1966)	Coordination compounds with metal-boron bonding	7 (31)	
10.5	G. A. Razuvaev and N. S. Vyazankin	<i>Pure Appl. Chem.</i> 19 , 353 (1969)	Organosilicon and organogermanium derivatives with silicon-metal and germanium-metal bonds	22 (72)	Lecture, 2nd Int. Symp. Organosilicon Chem., Bordeaux, 1968
10.6	G. Schmid	<i>Angew. Chem.</i> 82 , 920 (1970); <i>Angew. Chem. Int. Ed. Engl.</i> 9 , 819 (1970)	Metal-boron compounds—problems and perspectives	12 (89)	
10.7	N. S. Vyazankin, G. A. Razuvaev and O. A. Kruglaya	<i>Organometal. Chem. Rev.</i> 3 , 323 (1968)	Organometallic compounds with metal-metal bonds between different metals	101 (396)	

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|---|------------------------------------|---|--|-----------|---------------------------|
| 10.8 | J. F. Young | <i>Advan. Inorg. Chem. Radiochem.</i> 11 , 92 (1968) | Transition metal complexes with Group IVB elements | 62 (254) | |
| See also: A58.2 | | | | | |
| 11. <i>Compounds containing bonds between transition metals (including cluster compounds)</i> | | | | | |
| 11.1 | M. C. Baird | <i>Progr. Inorg. Chem.</i> 9 , 1 (1968) | Metal-metal bonds in transition metal complexes | 159 (898) | Most comprehensive survey |
| 11.2 | B. P. Biryukov and Y. T. Struchkov | <i>Usp. Khim.</i> 39 , 1672 (1970); <i>Russ. Chem. Rev.</i> 39 , 789 (1970) | Metal-metal bonds and covalent atomic radii of transition metals in their π -complexes and polycarbonyls | 15 (56) | |
| 11.3 | B. J. Bulkin and C. A. Rundell | <i>Coord. Chem. Rev.</i> 2 , 371 (1967) | Bonding in coordination compounds containing metal-metal bonds | 14 (85) | |
| 11.4 | P. Chini | <i>Inorg. Chim. Acta Rev.</i> 2 , 31 (1968) | The closed metal carbonyl clusters | 21 (223) | |
| 11.5 | P. Chini | <i>Pure Appl. Chem.</i> 24 , 489 (1970) | Some aspects of the chemistry of polynuclear metal carbonyl compounds | 15 (72) | Section lecture, 4ICOMC |
| 11.6 | F. A. Cotton | <i>Quart. Rev.</i> 20 , 389 (1966); <i>Usp. Khim.</i> 36 , 1799 (1967) | Transition metal compounds containing clusters of metal atoms | 13 (43) | |
| 11.7 | M. Czakis-Sulikowska and B. Kuznik | <i>Wiad. Chem.</i> 23 , 17 (1969) | Metal-metal bonds in chemical compounds | 18 (121) | Polish |
| 11.8 | J. Lewis | <i>Pure Appl. Chem.</i> 10 , 11 (1965); <i>Usp. Khim.</i> 36 , 847 (1967) | Metal-metal interaction in transition metal complexes | 26 (128) | Plenary lecture, 8ICCC |
| 11.9 | J. Lewis and R. S. Nyholm | <i>Sci. Progr.</i> 52 , 557 (1964) | Metal-metal bonds in transition metal complexes | 24 (111) | |
| 11.10 | E. L. Muetterties and C. M. Wright | <i>Quart. Rev.</i> 21 , 109 (1967) | Molecular polyhedra of high coordination number | 86 (404) | |

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
11. <i>Compounds containing bonds between transition metals (including cluster compounds) (cont'd)</i>					
11.11	B. Penfold	<i>Perspect. Struct. Chem.</i> 2, 71 (1968)	Stereochemistry of metal cluster compounds	79 (181)	Japan.
11.12	Y. Sasaki	<i>Kagaku No Ryoiki</i> 22, 906 (1968)	Metal-metal bonds in metal complexes	10 (38)	
11.13	K. L. Watters and W. M. Risen See also: 36.6	<i>Inorg. Chim. Acta Rev.</i> 3, 129 (1969)	Spectroscopic studies of metal-metal bonded compounds	26 (196)	
12. <i>Lewis Base complexes—general</i>					
12.1	G. R. Dobson, I. W. Stolz, and R. K. Sheline	<i>Advan. Inorg. Chem. Radiochem.</i> 8, 1 (1966)	Substitution products of the Group VIB metal carbonyls	82 (398)	Also includes extensive section on arene complexes
12.2	R. G. Hayter	<i>Prep. Inorg. React.</i> 2, 211 (1965)	Sulphur- and phosphorus-bridged complexes of transition metals	26 (69)	Many useful preparative details
12.3	T. A. Manuel	<i>Advan. Organometal. Chem.</i> 3, 181 (1965)	Lewis-base-metal carbonyl complexes	81 (373)	
13. <i>Lewis Base complexes—Group V donor atoms</i>					
13.1	G. Booth	<i>Advan. Inorg. Chem. Radiochem.</i> 6, 1 (1964)	Complexes of the transition metals with phosphines, arsines and stibines	69 (460)	Nickel complexes
13.2	A. B. Burg	<i>Accounts Chem. Res.</i> 2, 353 (1969)	Chemical consequences of fluoro-carbon phosphines	8 (61)	
13.3	P. S. Elmes and B. O. West	<i>Coord. Chem. Rev.</i> 3, 279 (1968)	The coordinating properties of pentamethylcyclopentaarsine	6 (12)	
13.4	T. Kruck	<i>Angew. Chem.</i> 79, 27 (1967); <i>Angew. Chem. Int. Ed. Engl.</i> 6, 53 (1967)	Trifluorophosphine complexes of transition metals	15 (94)	With metal carbonyls
13.5	B. O. West See also: A39.5	<i>Rec. Chem. Progr.</i> 30, 249 (1969)	Coordination chemistry of cyclic phosphines and arsines	11 (48)	

14. *Lewis Base complexes—Group VI donor atoms*

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|------|---|--|--|--------------|---|
| 14.1 | E. W. Abel and
B. C. Crosse | <i>Organometal. Chem.
Rev.</i> 2 , 443 (1967) | Sulphur-containing metal car-
bonyls | 52
(264) | |
| 14.2 | F. Bonati | <i>Organometal. Chem.
Rev.</i> 1 , 379 (1966) | Organometallic derivatives of β -
diketones | 11
(85) | |
| 14.3 | F. Bonati | <i>Stereochim. Inorg.,
Accad. Naz. Lincei,
Corso Estivo Chim.,
9th</i> , 1965 441 (1967) | Organometallic derivatives of β -
diketones | 13
(46) | See 14.2 above |
| 14.4 | J. A. McCleverty | <i>Progr. Inorg. Chem.</i>
10 , 49 (1968) | Metal 1,2-dithiolene and related
complexes | 173
(188) | |
| 14.5 | G. N. Schrauzer | <i>Transition Metal
Chem.</i> 4 , 299
(1968) | Coordination compounds of un-
saturated 1,2-dithiols and 1,2-
dithioketones | 37
(87) | |
| 14.6 | G. N. Schrauzer | <i>Accounts Chem. Res.</i>
2 , 72 (1969) | Coordination compounds with de-
localised ground states. The
transition metal derivatives of
dithiodiketones and ethylene-
1,2-dithiolates (Metal dithienes) | 9
(36) | |
| 14.7 | R. C. Mehrotra,
V. D. Gupta, and
D. Sukhani | <i>Inorg. Chim. Acta
Rev.</i> 2 , 111 (1968) | Thiol and thio- β -diketone deriva-
tives of the elements | 11
(241) | Includes transition metal π -com-
plex derivatives |
15. *Metal-carbon σ -bonds*
- | | | | | | |
|------|--------------|--|--|-------------|--|
| 15.1 | J. Chatt | <i>Rec. Chem. Progr.</i>
21 , 147 (1960) | Alkyl and aryl derivatives of transi-
tion metals | 11
(27) | |
| 15.2 | F. A. Cotton | <i>Chem. Rev.</i> 55 , 551
(1955) | Alkyls and aryls of transition
metals | 44
(168) | |
| 15.3 | R. J. Cross | <i>Inorg. Chim. Acta
Rev.</i> 3 , 75 (1969) | The effects of ligand and metal
hardness on the formation of
hydrido and organometallic com-
plexes by the β -interaction | 5
(52) | |

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
15. Metal-carbon σ -bonds (cont'd)					
15.4	D. Gibson	<i>Coord. Chem. Rev.</i> 4 , 225 (1969)	Carbon-bonded β -diketone complexes	16 (30)	
15.5	N. Hagihara and H. Yamazaki	<i>Kagaku No Ryoiki</i> 22 , 865 (1968)	Alkyl derivatives of transition metals	9 (43)	Japan.
15.6	H. Hashimoto	<i>Yuki Gosei Kagaku Kyokai Shi</i> 24 , 1156 (1966)	Some reactions of σ -bonded organometallic compounds	14 (87)	Japan. Nucleophilicity, electrophilicity and various reactions
15.7	R. F. Heck	<i>Advan. Chem. Ser.</i> 49 , 181 (1965)	Insertion reactions of metal complexes	39 (121)	
15.8	R. F. Heck	<i>Accounts Chem. Res.</i> 2 , 10 (1969)	Addition reactions of transition metal compounds	7 (36)	
15.9	I. I. Kritskaya	<i>Usp. Khim.</i> 35 , 393 (1969); <i>Russ. Chem. Rev.</i> 35 , 167 (1966)	Conditions for the formation and stabilisation of the carbon-transition metal σ -bonds	20 (192)	
15.10	M. F. Lappert and B. Prokai	<i>Advan. Organometal. Chem.</i> 5 , 225 (1967)	Insertion reactions of compounds of metals and metalloids involving unsaturated substrates	95 (294)	
15.11	R. Nast	<i>Angew. Chem.</i> 72 , 26 (1960)	Complex acetylides of transition metals	6 (29)	
15.12	G. W. Parshall	<i>Accounts Chem. Res.</i> 3 , 139 (1970)	Intramolecular aromatic substitution in transition metal complexes	6 (51)	The ortho-metalation 'reaction', mainly discussed in relation to phosphines
15.13	G. W. Parshall and J. J. Mrowca	<i>Advan. Organometal. Chem.</i> 7 , 157 (1968)	σ -Alkyl and σ -aryl derivatives of transition metals	53 (196)	
15.14	G. Razuvaev	<i>Tr. Khim. Khim. Tekhnol.</i> 278 (1963)	Homolytic decomposition reactions of organometallic compounds	11 (18)	Russ.

- | | | | | | |
|-------|--|---|--|-------------|--------|
| 15.15 | G. A. Razuvaev and
V. N. Latyaeva | <i>Usp. Khim.</i> 34 , 585
(1965); <i>Russ.</i>
<i>Chem. Rev.</i> 34 ,
251 (1965) | Covalent organometallic com-
pounds of the transition metals | 22
(70) | |
| 15.16 | A. M. Sladkov and
L. Y. Ukhin | <i>Usp. Khim.</i> 37 , 1750
(1968); <i>Russ.</i>
<i>Chem. Rev.</i> 37 ,
748 (1968) | Copper and silver acetylides in
organic synthesis | 16
(127) | |
| 15.17 | T. Takegami | <i>Kagaku To Kogyo</i>
(Tokyo) 20 , 1089
(1967) | Insertion reactions of organo-
metallic complexes | 15 | Japan. |
| 15.18 | J. S. Thayer | <i>Organometal. Chem.</i>
<i>Rev., Sect. A</i> 5 , 53
(1970) | Organoplatinum(IV) compounds | 14
(71) | |
| 15.19 | W. Tochtermann | <i>Angew. Chem.</i> 78 ,
355 (1966) | Structures and reactions of organic
"ate" complexes | 21
(183) | |
| 15.20 | M. Tsutsui | <i>Ann. N. Y. Acad.</i>
<i>Sci.</i> 125 , 147
(1965) | σ -Bonded organotransition metals
and diarene π -complexes | 7
(22) | |
| 15.21 | M. Tsutsui,
M. Hancock,
J. Ariyoshi, and
M. N. Levy | <i>Angew. Chem.</i> 81 ,
453 (1969);
<i>Angew. Chem. Int.</i>
<i>Ed. Engl.</i> 8 , 410
(1969) | Sigma-pi rearrangements of
organo-transition metal com-
pounds | 11
(108) | |

See also: A38.9; A39.4; A40.11; A48.1; E5.1; 4.10; 4.24; 4.30; 4.34

16. Fluorocarbon complexes

- | | | | | | |
|------|-----------------------------------|---|--|-------------|------------------|
| 16.1 | W. J. Bland | <i>Leicester Chem. Rev.</i>
8 , 15 (1967) | Fluorocarbon complexes of transi-
tion metals | 13
(20) | |
| 16.2 | M. I. Bruce and
W. R. Cullen | <i>Fluorine Chem. Rev.</i>
4 , 79 (1969) | The chemistry of fluorinated acetyl-
enes | 40
(191) | Esp. pp. 102-113 |
| 16.3 | M. I. Bruce and
F. G. A. Stone | <i>Prep. Inorg. React.</i> 4 ,
177 (1968) | Fluorocarbon complexes of transi-
tion metals | 59
(168) | |

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
16. Fluorocarbon complexes (cont'd)					
16.4	R. D. Chambers and T. Chivers	<i>Organometal. Chem. Rev.</i> 1 , 279 (1966); <i>Usp. Khim.</i> 36 , 1117 (1967)	Pentafluorophenyl-metal compounds	26 (65)	Esp. pp. 294-297
16.5	H. C. Clark	<i>Advan. Fluorine Chem.</i> 3 , 19 (1963)	Perfluoroalkyl derivatives of the elements	44 (180)	Transition metal compounds, p. 54
16.6	S. C. Cohen and A. G. Massey	<i>Advan. Fluorine Chem.</i> 6 , 185 (1970)	Polyfluoroaromatic derivatives of metals and metalloids	101 (332)	Esp. pp. 235-278
16.7	W. R. Cullen	<i>Fluorine Chem. Rev.</i> 3 , 73 (1969)	Fluoroalicyclic derivatives of metals and metalloids	56 (103)	
16.8	R. S. Nyholm	<i>Quart. Rev.</i> 24 , 1 (1970)	Transition metal complexes of some perfluoroligands	19 (33)	Presidential address (Chem. Soc.)
16.9	M. D. Rausch	<i>Ann. N.Y. Acad. Sci.</i> 28 , 611 (1966)	Fluorocarbon-transition metal chemistry	12 (50)	
16.10	F. G. A. Stone	<i>Endeavour</i> 25 , 33 (1966)	Fluorocarbon derivatives of transition metals	6 (18)	
16.11	P. M. Treichel and F. G. A. Stone	<i>Advan. Organometal. Chem.</i> 1 , 143 (1964)	Fluorocarbon derivatives of metals	78 (156)	
16.12	T. Wada	<i>Kagaku (Kyoto)</i> 18 , 144 (1963)	Fluorocarbon derivatives of metals	6 (41)	
See also: 7.1					
17. Complexes containing other halocarbons, or cyanocarbons					
17.1	W. H. Baddley	<i>Inorg. Chim. Acta Rev.</i> 2 , 7 (1968)	Percyanocarbon complexes of transition metals	11 (95)	
17.2	T. Chivers	<i>Organometal. Chem. Rev., Sect. A</i> 6 , 1 (1970)	Chlorocarbon and bromocarbon derivatives of metals and metalloids	64 (305)	Transition metals, pp. 41-54

18. *Hydrocarbon π -complexes—general reviews*

- | | | | | | |
|------|------------------------------------|--|--|------------|---------------------------------|
| 18.1 | N. Hagihara and
H. Yamazaki | <i>Yuki Gosei Kagaku
Kyokai Shi</i> 24 ,
1142 (1966) | Syntheses of organometallic π -
complexes | 14
(79) | Japan. |
| 18.2 | R. C. Kerber and
D. J. Ehntholt | <i>Synthesis</i> 449 (1970) | Transition metal complexes of
fulvenes | 17
(85) | |
| 18.3 | S. J. Lippard | <i>Ann. N. Y. Acad.
Sci.</i> 153 , 677
(1969) | Metal π -organic complexes: nature
of bonding and their role in
chemistry | 12
(37) | |
| 18.4 | P. L. Pauson | <i>Proc. Chem. Soc.</i> 297
(1960) | Hydrocarbon metal carbonyls | 9
(30) | Chemical Society Tilden Lecture |
| 18.5 | P. L. Pauson | <i>Endeavour</i> 21 , 175
(1962) | Hydrocarbon derivatives of transi-
tion metals | 8
(6) | |
| 18.6 | P. L. Pauson | <i>Pure Appl. Chem.</i> 17 ,
235 (1968) | Organometallic complexes of first-
row transition metals: some
recent advances | 18 | Plenary lecture, 31COMC |

See also: 36.1

19. *Hydrocarbon π -complexes—olefins and acetylenes*

- | | | | | | |
|------|---|--|--|-------------|--|
| 19.1 | M. A. Bennett | <i>Chem. Rev.</i> 62 , 611
(1962); <i>Usp. Khim.</i>
35 , 303 (1966) | Olefin and acetylene complexes of
transition elements | 42
(250) | |
| 19.2 | R. G. Guy and
B. L. Shaw | <i>Advan. Inorg. Chem.
Radiochem.</i> 4 , 78
(1962) | Olefin, acetylene and π -allylic
complexes of transition metals | 54
(223) | |
| 19.3 | F. R. Hartley | <i>Chem. Rev.</i> 69 , 799
(1969) | Olefin and acetylene complexes of
platinum and palladium | 46
(605) | Takes appropriate part ref. 19.1 to
July 1968 |
| 19.4 | L. J. Andrews | <i>Chem. Rev.</i> 54 , 713
(1954) | Aromatic molecular complexes of
the electron donor-acceptor type | 64
(331) | Including silver-olefin and -arene
complexes |
| 19.5 | U. Belluco,
B. Crociani,
R. Pietropaolo, and
P. Uguagliati | <i>Inorg. Chim. Acta
Rev.</i> 3 , 19 (1969) | Complexes of platinum(II) with
unsaturated hydrocarbons | 36
(253) | |

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
19. <i>Hydrocarbon π-complexes—olefins and acetylenes (cont'd)</i>					
19.6	G. F. Emerson, K. Ehrlich, W. P. Giering, and D. Ehntholt	<i>Trans. N. Y. Acad. Sci.</i> 30 , 1001 (1968)	The chemistry of olefin-iron carbonyl complexes	10 (33)	
19.7	E. O. Fischer and H. Werner	<i>Angew. Chem.</i> 75 , 57 (1963); <i>Angew. Chem. Int. Ed. Engl.</i> 2 , 80 (1963)	Metal π -complexes with di- and oligo-olefinic ligands	14 (187)	Expanded into book, ref. A23, A23a
19.8	K. A. Jensen	<i>Hauptjahrestag. Chem. Ges. DDR</i> 26 (1954)	The chemistry of olefin complexes	8 (27)	
19.9	R. Jones	<i>Chem. Rev.</i> 68 , 785 (1968)	Metal π -complexes with substituted olefins	22 (180)	Updates appropriate part of ref. 19.1
19.10	R. S. Nyholm	<i>Suom. Kemistilehti B</i> 42 , 165 (1969)	Structure and reactions of some chelated olefin complexes	5 (9)	Account of some of author's recent work
19.11	M. Orchin and P. J. Schmidt	<i>Inorg. Chim. Acta Rev.</i> 2 , 123 (1968)	Pyridine complexes of platinum(II)	13 (61)	Describes particular class of olefin complexes
19.12	M. Orchin and P. J. Schmidt	<i>Coord. Chem. Rev.</i> 3 , 345 (1968)	Pyridine-N-oxide complexes of platinum(II)	29 (43)	
19.13	G. Paiaro	<i>Stereochim. Inorg., Accad. Naz. Lincei, Corso Estivo Chim.</i> 9th , 1965 397 (1967)	Molecular asymmetry in π -bonded hydrocarbon metal compounds	11 (23)	
19.14	R. Pettit	<i>Ann. N. Y. Acad. Sci.</i> 125 , 89 (1965)	The chemical properties of olefin-iron π -complexes	9 (12)	
19.15	R. Pettit and G. F. Emerson	<i>Advan. Organometal. Chem.</i> 1 , 1 (1964)	Diene-iron carbonyl complexes and related species	46 (134)	
19.16	R. Pettit, G. F. Emerson, and J. Mahler	<i>J. Chem. Educ.</i> 40 , 175 (1963)	Chemistry of the diene-iron tricarbonyl complexes	7 (13)	

- 19.17 H. W. Quinn and J. H. Tsai *Advan. Inorg. Chem. Radiochem.* **12**, 217 (1969) Olefin complexes of the transition metals 157 (631) Exhaustive survey, revising appropriate part of ref. 19.2
- 19.18 F. L. Bowden and A. B. P. Lever *Organometal. Chem. Rev.* **3**, 227 (1968) The transition metal chemistry of acetylenes 53 (197) Complements refs. A39.2, A39.3

See also: A22; A23; A23a; A24; A37.1; A39.2; A39.3; A44.1; A44.2; A46.1; 4.38; 6.17; 6.18; 22.10; 28.7; 28.18; 28.19

20. *Hydrocarbon π -complexes—allyl*

- 20.1 L. A. Fedorov *Usp. Khim.* **39**, 1389 (1970); *Russ. Chem. Rev.* **39**, 655 (1970) Nuclear magnetic resonance spectroscopy of organometallic allyl compounds 18 (171)
- 20.2 E. O. Fischer and H. Werner *Z. Chem.* **2**, 174 (1962) Transition metal complexes with π -allyl and π -enyl ligands 12 (59)
- 20.3 M. L. H. Green and P. L. I. Nagy *Advan. Organometal. Chem.* **2**, 325 (1964) Allyl metal complexes 39 (106)
- 20.4 M. I. Lobach, B. D. Babitskii, and V. A. Kormer *Usp. Khim.* **36**, 1158 (1967); *Russ. Chem. Rev.* **36**, 476 (1967) π -Allyl complexes of the transition metals 23 (318)
- 20.5 S. Otsuka *Kagaku No Ryoiki, Zokan* 225 (1970) Chemistry of coordination complexes and organometallic compounds. Allyl and enyl complexes 40 (135) Japan. Allyl complexes classified by symmetry, and discussions of NMR and solution dynamics
- 20.6 G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, and H. Zimmermann *Angew. Chem.* **78**, 157 (1966); *Angew. Chem. Int. Ed. Engl.* **5**, 151 (1966); *Usp. Khim.* **37**, 1056 (1968) Allyl-transition metal systems 14 (44)

See also: 19.2; 28.4; 28.6; 28.12; 28.32; 28.33

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
21. <i>Hydrocarbon π-complexes—cyclobutadiene</i>					
21.1	R. Criegee	<i>Angew. Chem.</i> 74 , 703 (1962); <i>Angew. Chem. Int. Ed. Engl.</i> 1 , 519 (1962)	Attempts to synthesise tetramethylcyclobutadiene	9 (38)	
21.2	R. Criegee	<i>Bull. Soc. Chim. Fr.</i> 1 (1965)	The problem of cyclobutadiene	6 (40)	
21.3	P. M. Maitlis	<i>Advan. Organometal. Chem.</i> 4 , 95 (1966)	Cyclobutadiene-metal complexes	49 (95)	
21.4	R. Pettit	<i>Pure Appl. Chem.</i> 17 , 253 (1968)	Cyclobutadiene and its metal complexes	20 (25)	Plenary lecture, 3ICOMC
21.5	L. Watts and R. Pettit	<i>Advan. Chem. Ser.</i> 62 , 549 (1967)	Chemistry of cyclobutadiene-iron tricarbonyl	6 (7)	
See also: A53					
22. <i>Hydrocarbon π-complexes—cyclopentadienyl and arene</i>					
22.1	E. O. Fischer and H. P. Fritz	<i>Advan. Inorg. Chem. Radiochem.</i> 1 , 56 (1959)	Compounds of aromatic ring systems and metals	60 (232)	Review of pioneering work
22.2	R. L. Pruett	<i>Prep. Inorg. React.</i> 2 , 187 (1965)	Cyclopentadienyl and arene metal carbonyls	23 (87)	
22.3	G. Wilkinson and F. A. Cotton	<i>Progr. Inorg. Chem.</i> 1 , 1 (1959); <i>Usp. Khim.</i> 31 , 838 (1962)	Cyclopentadienyl and arene metal compounds	124 (399)	Review of pioneering work
22.4	J. M. Birmingham	<i>Chem. Eng. Progr.</i> 58 (10), 74 (1962)	Cyclopentadienyl compounds of metals	5 (102)	
22.5	J. M. Birmingham	<i>Advan. Organometal. Chem.</i> 2 , 365 (1964)	Synthesis of cyclopentadienyl metal compounds	49 (425)	Synthetic methods detailed

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| 22.6 | E. O. Fischer | <i>Angew. Chem.</i> 67 ,
475 (1955) | Metal compounds of cyclopenta-
diene and indene | 8
(59) | |
| 22.7 | W. F. Little | <i>Survey Progr. Chem.</i>
1 , 133 (1963) | Metallocenes | 78
(244) | |
| 22.8 | M. D. Rausch | <i>J. Chem. Educ.</i> 37 ,
568 (1960) | Cyclopentadienyl compounds of
metals and metalloids | 11
(118) | |
| 22.9 | E. O. Fischer and
H. P. Fritz | <i>Angew. Chem.</i> 73 ,
353 (1961) | π -Complexes of benzene systems
with transition metals | 12
(163) | |
| 22.10 | T. Ogura and
S. Kawaguchi | <i>Kagaku (Kyoto)</i> 23 ,
1105 (1968) | Dewar-benzene transition metal
complexes | 6
(30) | Japan. |
| 22.11 | S. Rosca | <i>Stud. Cercet. Chim.</i>
17 , 613 (1969) | Benzenoid-metal aromatic π -com-
plexes | 24
(78) | Rom. |
| 22.12 | M. Tsutsui | <i>Nippon Kagaku
Zasshi</i> 88 , 1013
(1967) | Chemistry of drum-shaped π -com-
plexes. Its significance in catalysis | 17
(31) | Japan. |
| 22.13 | M. Tsutsui | <i>Trans. N.Y. Acad.
Sci.</i> 30 , 658 (1968) | Arene π -complex chemistry | 9
(31) | |
- See also: A25; A38.7; A38.8; A48.1; A49.1; A57.3; 12.1; 15.20
23. *Hydrocarbon π -complexes—larger rings*
- | | | | | | |
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| 23.1 | M. A. Bennett | <i>Advan. Organometal.
Chem.</i> 4 , 353 (1966) | Metal π -complexes formed by
seven-membered and eight-
membered carbocyclic com-
pounds | 35
(138) | |
| 23.2 | M. R. Churchill | <i>Progr. Inorg. Chem.</i>
11 , 53 (1970) | Transition metal complexes of
azulene and related ligands | 46
(113) | |
24. *Hydrocarbon π -complexes—fluxional molecules*
- | | | | | | |
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| 24.1 | S. J. Lippard | <i>Trans. N.Y. Acad.
Sci.</i> 29 , 917 (1967) | Stereochemically dynamic organo-
metallic compounds | 3
(18) | |
| 24.2 | F. A. Cotton | <i>Chem. Brit.</i> 4 , 345
(1968) | Fluxional organometallic molecules | 4
(15) | |
| 24.3 | F. A. Cotton | <i>Accounts Chem. Res.</i>
1 , 257 (1968) | Fluxional organometallic molecules | 9
(49) | Author's work reviewed |

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
<i>25. Organic chemistry of metallocenes</i>					
25.1	K. Arakawa and K. Yamakawa	<i>Kagaku No Ryoiki</i> 14 , 632 (1960)	Chemistry of metallocenes	83 (116)	Japan.
25.2	D. Braun	<i>Angew. Chem.</i> 73 , 197 (1961); <i>Usp. Khim.</i> 31 , 769 (1962)	Macromolecular organometallic compounds	12 (132)	Including ferrocene derivatives
25.3	D. E. Bublitz and K. E. Rinehart	<i>Org. React.</i> 17 , 1 (1969)	Synthesis of substituted ferrocenes and other π -cyclopentadienyl transition metal compounds	154 (659)	Comprehensive survey including most known ring-substituted derivatives
25.4	M. Cais	<i>Record Chem. Progr.</i> 27 , 177 (1966)	Some carbonium ions of unusual stability	22 (28)	Refs. 25.4 and 25.5 are essentially the same article
25.5	M. Cais	<i>Organometal. Chem. Rev.</i> 1 , 435 (1966)	The problem of metal participation in the properties of α -metallocenyl-carbonium ions	20 (27)	
25.6	H. Falk	<i>Oesterr. Chem. Ztg.</i> 66 , 242 (1965)	Determination of absolute configurations of axial- and planar-symmetrical compounds	11 (43)	
25.7	N. Hagihara and H. Yamazaki	<i>Kagaku (Kyoto)</i> 14 , 373 (1959)	Ferrocene-type complex compounds and organic synthesis	8 (44)	Japan. Symposium on ferrocene chemistry: see also refs. 25.9, 25.42
25.8	H. Imai	<i>Kagaku (Kyoto)</i> 25 , 430, 519, 628 (1970)	Chemistry of ferrocenes	12 + 10 (141)	Japan. I, Preparation, properties; cetylation, carboxylation; II, Acetylferrocenecarboxylates; III, Acid derivatives; metalation, arylation
25.9	M. Kumada	<i>Kagaku (Kyoto)</i> 14 , 364 (1959)	Synthesis and properties of ferrocene	10	Japan. See also refs. 25.7, 25.42
25.10	J. K. Lindsay	<i>Org. Chem. Bull. (Kodak)</i> 30 , No. 3 (1958)	Ferrocene	4 (29)	

25.11	H. J. Lorkowski	<i>Fortschr. Chem. Forsch.</i> 9 , 207 (1967)	Ferrocene as a foundation stone of macro-molecular chemistry	47 (105)	Polymers containing ferrocene
25.12	J. M. Mallan and R. L. Bebb	<i>Chem. Rev.</i> 69 , 693 (1969)	Metalations by organolithium compounds	63 (630)	Ferrocene, etc. pp. 713, 739
25.13	A. N. Nesmeyanov	<i>Proc. Roy. Soc. Ser. A</i> 246 , 495 (1958)	Substitutions in the ferrocene nucleus	9 (17)	
25.14	A. N. Nesmeyanov	<i>Zh. Vses. Khim. Obshch.</i> 7 , 249 (1962)	Chemistry of ferrocene	15 (3)	Russ.
25.15	A. N. Nesmeyanov	<i>Bull. Soc. Chim. Fr.</i> , 1229 (1965)	Peculiarities of ferrocene chemistry and of the "sandwich" structure	11 (64)	
25.16	A. N. Nesmeyanov	<i>Pure Appl. Chem.</i> 17 , 211 (1968)	Recent developments in the organic chemistry of ferrocene	24 (13)	Plenary lecture, 3ICOMC
25.17	A. N. Nesmeyanov and E. G. Perevalova	<i>Khim. Nauka Prom.</i> 3 , 146 (1958)	Ferrocene as an aromatic system	13 (124)	Russ.
25.18	A. N. Nesmeyanov and E. G. Perevalova	<i>Usp. Khim.</i> 27 , 3 (1958)	Cyclopentadienyl compounds of metals and related compounds	54 (219)	Russ. Mainly organic chemistry of ferrocene
25.19	A. N. Nesmeyanov and E. G. Perevalova	<i>Ann. N.Y. Acad. Sci.</i> 125 , 67 (1965)	Recent advances in ferrocene chemistry in the USSR	22 (132)	
25.20	E. W. Neuse	<i>Advan. Macromol. Chem.</i> 1 , 1 (1968)	Ferrocene polymers	138 (351)	
25.21	E. W. Neuse	<i>Encycl. Polymer Sci. Technol.</i> 8 , 667 (1967)	Metallocene polymers	26 (112)	
25.22	P. L. Pauson	<i>Quart. Rev.</i> 9 , 391 (1955)	Ferrocene and related compounds	24 (88)	
25.23	C. U. Pittman	<i>J. Paint Technol.</i> 39 , 585 (1967)	Ferrocene-containing polymers—potential applications	8 (114)	

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Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
25. <i>Organic chemistry of metallocenes (cont'd)</i>					
25.24	K. Plesske	<i>Angew. Chem.</i> 74 , 301, 347 (1962); <i>Angew. Chem. Int. Ed. Engl.</i> 1 , 312 (1962)	Ring-substitutions and secondary reactions of aromatic π -complexes I, II	16 + 6 (267)	
25.25	M. D. Rausch	<i>Can. J. Chem.</i> 41 , 1289 (1963)	Metallocene chemistry—a decade of progress	26 (152)	
25.26	M. D. Rausch	<i>Advan. Chem. Ser.</i> 37 , 56 (1963)	Ring substitution reactions of metal cyclopentadienyls and metal arenes	22 (129)	
25.27	M. D. Rausch	<i>J. Paint Technol.</i> 39 , 576 (1967)	Metallocene chemistry	9 (63)	
25.28	M. D. Rausch and J. M. Birmingham	<i>Ann. N.Y. Acad. Sci.</i> 125 , 57 (1965)	Synthesis of metallocenes	10 (103)	
25.29	M. D. Rausch, M. Vogel, and H. Rosenberg	<i>J. Chem. Educ.</i> 34 , 268 (1957)	Ferrocene: a novel organometallic compound	5 (51)	
25.30	M. Rosenblum and F. W. Abbate	<i>Advan. Chem. Ser.</i> 62 , 532 (1967)	The role of the metal atom in the reactions of the iron group metallocenes	17 (69)	
25.31	K. Schlögl	<i>Oesterr. Chem. Ztg.</i> 59 , 93 (1958)	Ferrocene and related metal cyclopentadienyls	12 (73)	
25.32	K. Schlögl	<i>Fortschr. Chem. Forsch.</i> 6 , 479 (1966)	Stereochemistry of metallocenes	36 (82)	
25.33	K. Schlögl	<i>Topics Stereochem.</i> 1 , 39 (1967)	Stereochemistry of metallocenes	53 (120)	Expansion of ref. 25.32
25.34	K. Schlögl	<i>Pure Appl. Chem.</i> 24 , 413 (1970); <i>Usp. Khim.</i> 39 , 1424 (1970)	Configurational and conformational studies in the metallocene field	20 (33)	Section lecture, 4ICOMC

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| 25.35 | V. N. Setkina and
D. N. Kursanov | <i>Usp. Khim.</i> 37 , 1729
(1968); <i>Russ. Chem.
Rev.</i> 37 , 737 (1968) | Isotopic exchange of hydrogen in
aromatic complexes of the transi-
tion metals | 11
(87) | Ferrocenes, cymantrenes, etc. |
| 25.36 | D. W. Slocum, T. R.
Engelmann,
C. Ernst, C. A.
Jennings, W. Jones,
B. Koonsivitsky,
J. Lewis, and
P. Shenkin | <i>J. Chem. Educ.</i> 46 ,
144 (1969) | Metalation of metallocenes | 7
(63) | |
| 25.37 | S. Swaminathan and
S. Ranganathan | <i>Curr. Sci.</i> 25 , 6
(1956) | The chemistry of ferrocene and
related compounds | 3
(31) | |
| 25.38 | H. Valot | <i>Peintures, Pigments,
Vernis</i> 37 , 444
(1961) | The chemistry of ferrocene | 6 | |
| 25.39 | T. P. Vishnyakova,
I. A. Golubeva, and
T. A. Sokolinskaya | <i>Usp. Khim.</i> 36 , 2136
(1967); <i>Russ.
Chem. Rev.</i> 36 ,
932 (1967) | Polymers based on ferrocene | 14
(108) | |
| 25.40 | W. E. Watts | <i>Organometal. Chem.
Rev.</i> 2 , 231 (1967) | Ferrocenophane systems | 24
(91) | |
| 25.41 | K.-L. Wu | <i>Hua Hsueh T'ung
Pao</i> 293 (1963) | Organosilicon derivatives of ferro-
cene | 9
(21) | Japan. |
| 25.42 | S. Yamada | <i>Kagaku (Kyoto)</i> 14 ,
358 (1959) | Structure and bonding in ferrocene
and allied compounds | 7
(63) | Japan. Symp. on ferrocene chemi-
stry, see also refs. 25.7, 25.9 |
- See also: A26; A48.2; A49.1; A50.1; A59; 1.13; 22.7; 34.5
26. *Metallocarborane complexes*
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| 26.1 | M. F. Hawthorne | <i>Endeavour</i> 25 , 146
(1966) | Polyhedral boranes, carboranes
and carbametallic boron hydride
derivatives | 8
(40) |
| 26.2 | M. F. Hawthorne | <i>Accounts Chem. Res.</i>
1 , 281 (1968) | The chemistry of the polyhedral
species derived from transition
metals and carboranes | 8
(40) |

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Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
26. Metallocarborane complexes (cont'd)					
26.3	M. F. Hawthorne	<i>Pure Appl. Chem.</i> 17 , 195 (1968)	Recent developments in the chemistry of polyhedral complexes derived from transition metals and carboranes	16 (27)	Plenary lecture, 3ICOMC
26.4	L. J. Todd	<i>Advan. Organometal. Chem.</i> 8 , 87 (1970)	Transition metal-carborane complexes	29 (49)	
26.5	L. J. Todd	<i>Progr. Boron. Chem.</i> 2 , 1 (1970)	The chemistry of polyhedral borane ions	35 (81)	
	See also: A51				
27. Kinetics and mechanisms					
27.1	R. J. Angelici	<i>Organometal. Chem. Rev.</i> 3 , 173 (1968)	Kinetics and mechanisms of substitution reactions of metal carbonyl complexes	54 (103)	
27.2	F. Basolo	<i>Pure Appl. Chem.</i> 17 , 37 (1968)	Substitution reactions of metal complexes	18 (55)	Tetrahedral carbonyls and nitrosyl-carbonyls. Lecture 10ICCC
27.3	D. A. Brown	<i>Inorg. Chim. Acta Rev.</i> 1 , 35 (1967)	Substitution reactions of metal carbonyl compounds	13 (76)	
27.4	J. L. Burmeister and F. Basolo	<i>Prep. Inorg. React.</i> 5 , 1 (1968)	Application of reaction mechanisms to the synthesis of coordination compounds	43 (211)	
27.5	K. Moedritzer	<i>Advan. Organometal. Chem.</i> 6 , 171 (1968)	Redistribution equilibria of organometallic compounds	101 (316)	Transition metals, pp. 256-262
27.6	G. A. Razuvaev	<i>Zh. Vses. Khim. Obshch.</i> 7 , 325 (1962)	Free radicals in reactions of organometallic compounds	7 (16)	Survey of author's work
27.7	W. Strohmeier	<i>Fortschr. Chem. Forsch.</i> 10 , 306 (1968)	Kinetics and mechanism of exchange and substitution reactions in metal carbonyls	41 (49)	

- 27.8 H. Werner *Angew. Chem.* **80**, 1017 (1968); *Angew. Chem. Int. Ed. Engl.* **7**, 930 (1968) Kinetic studies on substitution reactions of carbonylmetal complexes 12 (106)

See also: A54

28. *Organic synthesis via organometallics*

Topics covered by references in Sections 28 and 29 are often closely related, and the location of particular review sometimes arbitrary.

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|------|--|--|---|----------|------------------------|
| 28.1 | A. Aguiló | <i>Advan. Organometal. Chem.</i> 5 , 321 (1967) | Olefin oxidation with palladium(II) catalyst in solution | 32 (85) | |
| 28.2 | C. W. Bird | <i>Chem. Rev.</i> 62 , 283 (1962); <i>Usp. Khim.</i> 33 , 1304 (1964) | Synthesis of organic compounds by direct carbonylation reactions using metal carbonyls | 20 (206) | Expanded into ref. A30 |
| 28.3 | K. Bittler, N. von Kutepow, D. Neubauer, and H. Reis | <i>Angew. Chem.</i> 80 , 352 (1968); <i>Angew. Chem. Int. Ed. Engl.</i> 7 , 329 (1968) | Carbonylation of olefins under mild temperature conditions in the presence of palladium complexes | 7 (21) | |
| 28.4 | B. Bogdanovic, P. Heimbach, K. Tanaka, and G. Wilke | <i>Magyar Kem. Lapja</i> 5 , 237 (1966) | Reactions of olefins and diolefins on nickel complexes | 5 | Hung. |
| 28.5 | G. P. Chiusoli | <i>Bull. Soc. Chim. Fr.</i> 1139 (1969) | Coordination and specificity in new organic syntheses | 9 (83) | |
| 28.6 | G. P. Chiusoli and L. Cassar | <i>Angew. Chem.</i> 79 , 177 (1967); <i>Angew. Chem. Int. Ed. Engl.</i> 6 , 124 (1967) | Nickel-catalysed reactions of allyl halides and related compounds | 10 (55) | |
| 28.7 | N. Hagihara | <i>Yuki Gosei Kagaku Kyokai Shi</i> 19 , 20 (1961) | Cyclisation of acetylenic compounds in the presence of organometallic compounds | 9 (45) | Japan. |

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
28. <i>Organic synthesis via organometallics (cont'd)</i>					
28.8	N. Hagihara	<i>Kogyo Kagaku Zasshi</i> 66 , 1022 (1963)	Use of organometallic complexes in synthetic chemistry	5 (44)	Japan.
28.9	N. Hagihara	<i>Yuki Gosei Kagaku Kyokai Shi</i> 22 , 513 (1964)	Some organometallic complexes in organic synthesis	7 (36)	Japan.
28.10	N. Hagihara	<i>Kobunshi</i> 16 , 531 (1967)	Application of organometallic complexes to synthetic chemistry	7 (33)	Japan. Activation of small molecules, template reactions, coordination of unstable molecules and radicals
28.11	H. Hashimoto	<i>Kagaku To Kogyo (Tokyo)</i> 20 , 1077 (1967)	Oxidation by organometallic complexes	6	Japan. Organopalladium compounds
28.12	P. Heimbach, P. W. Jolly, and G. Wilke	<i>Advan. Organometal. Chem.</i> 8 , 29 (1970)	π -Allyl-nickel intermediates in organic synthesis	58 (121)	
28.13	Y. T. Huang	<i>Hua Hsueh T'ung Pao</i> No. 1, 1 (1964)	Recent progress in the applications of metalorganic compounds in organic synthesis	16 (128)	Japan.
28.14	A. Misono and I. Ogata	<i>Kagaku To Kogyo (Tokyo)</i> 20 , 1083 (1967)	Reduction by organometallic complexes	8	Japan. Activation of molecular hydrogen and of substrate, followed by reaction
28.15	T. Mizoroki	<i>Yuki Gosei Kagaku Kyokai Shi</i> 28 , 697 (1970)	Carbonylation reactions catalysed by metal carbonyls	11 (60)	Japan. Esp. cobalt and nickel
28.16	I. Moritani and Y. Fujiwara	<i>Kagaku To Kogyo (Tokyo)</i> 21 , 751 (1968)	Organic synthesis by organometallic complexes. Aromatic substitution of olefins by palladium salts	6 (15)	Japan.

28.17	A. Nakamura	<i>Kagaku No Ryoiki</i> 22, 418 (1968)	Reactions and catalytic action of metal complexes. Complexes of allene and acetylene and their catalytic polymerisation	15 (68)	Japan.
28.18	V. O. Reikhsfel'd and K. L. Makovetskii	<i>Usp. Khim.</i> 35, 1204 (1966); <i>Russ.</i> <i>Chem. Rev.</i> 35, 510 (1966)	The cyclisation of alkynes and their derivatives	14 (121)	By transition metal complexes
28.19	W. Reppe, N. von Kutepow, and A. Magin	<i>Angew. Chem.</i> 81, 717 (1969); <i>Angew.</i> <i>Chem. Int. Ed.</i> <i>Engl.</i> 7, 727 (1969)	Cyclisation of acetylenic compounds	7 (21)	
28.20	M. Ryang	<i>Organometal. Chem.</i> <i>Rev., Sect. A</i> 5, 67 (1970)	Metal carbonyls as stoichiometric reagents in organic synthesis	27 (88)	
28.21	Y. Saito	<i>Yuki Gosei Kagaku</i> <i>Kyokai Shi</i> 26, 946 (1968)	Oxidation by oxygen complexes and oxy-metal ions	11 (86)	Japan.
28.22	G. N. Schrauzer, P. Glockner, and S. Eichler	<i>Angew. Chem.</i> 76, 28 (1964); <i>Angew.</i> <i>Chem. Int. Ed.</i> <i>Engl.</i> 3, 185 (1964)	Coordination chemistry and catalysis—investigations on the synthesis of cyclooctatetraene by the method of W. Reppe	7 (35)	
28.23	J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, R. Rüttingen, and H. Kojer	<i>Angew. Chem.</i> 71, 176 (1959)	Catalytic reactions of olefins with platinum metal compounds	7 (17)	
28.24	J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, and A. Sabel	<i>Angew. Chem.</i> 74, 93 (1962); <i>Angew.</i> <i>Chem. Int. Ed.</i> <i>Engl.</i> 1, 80 (1962)	Palladium chloride-catalysed oxidation of olefins	9 (19)	

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Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
28. <i>Organic synthesis via organometallics (cont'd)</i>					
28.25	E. W. Stern	<i>Catal. Rev.</i> 1 , 73 (1967)	Reactions of unsaturated ligands in palladium(II) complexes	80 (224)	
28.26	H. W. Sternberg, R. Markby, and I. Wender	<i>Chim. Ind. (Milan)</i> 42 , 41 (1960)	Metal carbonyls and analogous compounds as catalytic intermediates in organic syntheses	11 (63)	
28.27	J. Tsuji	<i>Nippon Kagaku Zasshi</i> 88 , 687 (1967)	Organic syntheses by means of noble metal compounds	20 (59)	Japan. Review of author's work on palladium-olefin complexes and nucleophiles
28.28	J. Tsuji	<i>Accounts Chem. Res.</i> 2 , 144 (1969)	Carbon-carbon bond formation via palladium complexes	9 (86)	
28.29	J. Tsuji	<i>Advan. Org. Chem.</i> 6 , 109 (1969)	Organic syntheses by means of noble metal compounds	147 (346)	
28.30	M. Tsutsui	<i>Ann. N. Y. Acad. Sci.</i> 137 , 205 (1966)	Organometallics as preparative intermediates	12 (12)	
28.31	N. von Kutepow and H. Kindler	<i>Angew. Chem.</i> 72 , 802 (1960)	The alcohol synthesis of W. Reppe	4 (16)	
28.32	G. Wilke	<i>Angew. Chem.</i> 75 , 10 (1963); <i>Angew. Chem. Int. Ed. Engl.</i> 2 , 105 (1963); <i>Usp. Khim.</i> 33 , 687 (1964)	Cyclooligomerisation of butadiene and transition metal π -complexes	11 (48)	
28.33	G. Wilke, B. Bogdanovic, P. Heimbach, M. Kröner, and E. W. Müller	<i>Advan. Chem. Ser.</i> 34 , 137 (1962)	Reactions of new π -complex catalysts	8 (11)	
28.34	H. H. Zeiss	<i>Bull. Soc. Chim. Fr.</i> 1500 (1963)	Coordination synthesis on metal centres	7	

- 28.35 K. Ziegler *Ind. Chim. Belge (Suppl.)* **1**, 40 (1959) Metalorganic compounds as intermediates and catalysts 6 (38)

See also: A30; A39.3; A39.4; E5.2; 4.32; 4.33; 15.16

29. Catalysis by organometallics

Topics covered by references in Sections 28 and 29 are often closely related, and the location of a particular review is sometimes arbitrary

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| 29.1 | U. Birkenstock,
H. Bönemann,
B. Bogdanovic,
D. Walter, and
G. Wilke | <i>Advan. Chem. Ser.</i>
70 , 250 (1968) | π -Allylnickel compounds as homogeneous catalysts | 16
(25) | |
| 29.2 | G. C. Bond | <i>Platinum Metals Rev.</i>
8 , 92 (1964) | Platinum metal salts and complexes as homogeneous catalysts | 7
(28) | |
| 29.3 | G. C. Bond | <i>Advan. Chem. Ser.</i>
70 , 25 (1968) | Homogeneous and heterogeneous catalysis by noble metals | 10
(16) | |
| 29.4 | G. C. Bond | <i>Annu. Rep. Progr. Chem.</i> 63 , 27 (1967); <i>Usp. Khim.</i> 37 , 1694 (1968) | Homogeneous catalysis by complexes of the Group VIII elements | 17
(141) | |
| 29.5 | G. C. Bond and
P. B. Wells | <i>Advan. Catal.</i> 15 , 92 (1964) | The mechanism of the hydrogenation of unsaturated hydrocarbons on transition metal catalysts | 135
(161) | Esp. pp. 205 ff: The hydrocarbon-metal bond in catalytic and organometallic chemistry |
| 29.6 | S. Carra and R. Ugo | <i>Inorg. Chim. Acta Rev.</i> 1 , 49 (1967) | Coordination and olefin catalysis by transition metals | 15
(80) | |
| 29.7 | A. J. Chalk | <i>Trans. N. Y. Acad. Sci.</i> 32 , 481 (1970) | Olefin hydrosilation catalysed by Group VIII metal complexes | 8 | |
| 29.8 | J. P. Collman | <i>Accounts Chem. Res.</i> 1 , 136 (1968) | Patterns of organometallic reactions related to homogeneous catalysis | 8
(86) | |

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Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
29. <i>Catalysis by organometallics (cont'd)</i>					
29.9	J. P. Collman	<i>Trans. N. Y. Acad. Sci.</i> 30 , 479 (1968)	The role of vacant coordination sites in homogeneous catalysis	4 (13)	
29.10	R. Cramer	<i>Accounts Chem. Res.</i> 1 , 186 (1968)	Transition metal catalysis exemplified by some rhodium-promoted reactions of olefins	6 (28)	
29.11	N. R. Davies	<i>Rev. Pure Appl. Chem.</i> 17 , 83 (1967)	Isomerisation of olefins catalysed by palladium and other transition-metal complexes	11 (34)	
29.12	V. N. Davydov	<i>Chem. Tech. (Leipzig)</i> 8 , 431 (1959)	Hydrogenation reaction with cobalt carbonyl hydride as a hydrogenation agent	10 (29)	
29.13	J. L. Garnett and W. A. Sollich-Baumgartner	<i>Advan. Catal.</i> 16 , 95 (1966)	π -Complex adsorption in hydrogen exchange on Group VIII transition metal catalysts	27 (45)	
29.14	J. Halpern	<i>Ann. Rev. Phys. Chem.</i> 16 , 103 (1965)	Catalysis by coordination compounds	22 (131)	Particularly ruthenium
29.15	J. Halpern	<i>Advan. Chem. Ser.</i> 70 , 1 (1968)	Homogeneous catalysis by coordination compounds	24 (92)	
29.16	J. Halpern	<i>Pure Appl. Chem.</i> 20 , 59 (1969)	Coordination compounds in homogeneous catalysis	17 (44)	Plenary lecture, 8ICCC
29.17	A. J. Hubert and H. Reimlinger	<i>Synthesis</i> 405 (1970)	The isomerisation of olefins. Thermal and catalytic isomerisation of olefins using acids, metals, metal complexes or boron compounds as catalysts	26 (326)	Esp. pp. 408-413
29.18	B. R. James	<i>Coord. Chem. Rev.</i> 1 , 505 (1966)	Reactions and catalytic properties of rhodium complexes in solution	20 (160)	
29.19	J. Kwiatek	<i>Catal. Rev.</i> 1 , 37 (1967)	Reactions catalysed by pentacyanocobaltate(II)	36 (114)	

29.20	H. Müller, D. Wittenberg, H. Seibt, and E. Scharf	<i>Angew. Chem.</i> 77 , 318 (1965); <i>Angew. Chem. Int. Ed. Engl.</i> 4 , 327 (1965)	Recent results in the catalytic oli- gomerisation and cooligomerisa- tion of butadiene	6 (35)	
29.21	E. I. Ochiai	<i>Coord. Chem. Rev.</i> 3 , 49 (1968)	Catalytic functions of metal ions and their complexes	41 (130)	
29.22	M. Orchin	<i>Advan. Catal.</i> 16 , 1 (1966)	The homogeneous catalytic isomer- isation of olefins by transition metal catalysts	47 (72)	
29.23	J. A. Osborn	<i>Endeavour</i> 26 , 144 (1967)	Homogeneous catalysis	5 (14)	
29.24	G. N. Schrauzer	<i>Advan. Catal.</i> 18 , 373 (1968)	On transition-metal catalysed reac- tions of norbornadiene and the concept of π -complex multi- centre processes	24 (60)	
29.25	W. Strohmeier	<i>Struct. Bonding (Berlin)</i> 5 , 96 (1968)	Problem and model of homogeneous catalysis	22 (32)	
29.26	G. Szonyi	<i>Advan. Chem. Ser.</i> 70 , 53 (1968)	Recent homogeneously-catalysed commercial processes	44 (42)	
29.27	M. Tsutsui, J. Ariyoshi, T. Koyano, and M. N. Levy	<i>Advan. Chem. Ser.</i> 70 , 266 (1968)	Catalysis at the atomic level	12 (17)	
29.28	R. Ugo	<i>Chim. Ind. (Milan)</i> 51 , 1319 (1969)	General features of homogeneous catalysis with transition metals	13	Esp. π -hydrocarbon-metal com- plexes
29.29	M. E. Vol'pin and I. S. Kolomnikov	<i>Usp. Khim.</i> 38 , 561 (1969); <i>Russ. Chem. Rev.</i> 38 , 273 (1969)	Homogeneous hydrogenation	17 (282)	
29.30	K. Wada and H. Hashimoto	<i>Senryo To Yakuhin</i> 12 , 431 (1967)	Copper-catalysed reactions	8 (119)	Japan.

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Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
29. <i>Catalysis by organometallics (cont'd)</i>					
29.31	D. E. Webster and P. B. Wells	<i>Platinum Metals Rev.</i> 13 , 104 (1969)	Homogeneous catalysis by some ruthenium and rhodium complexes	7 (8)	
29.32	G. Wilkinson	<i>Bull. Soc. Chim. Fr.</i> 5055 (1968)	Homogeneous hydrogenation and hydroformylation of olefins by rhodium-triphenylphosphine catalysts	4 (10)	
29.33	A. Yamamoto	<i>Sekiyu Gakkai Shi</i> 8 , 930 (1965)	Organometallic compounds and their catalysing effects	5 (18)	Japan. Polymerisation, hydrogenation, isomerisation, hydroformylation
See also: A55.2; 4.23; 4.25; 22.12; 35.9					
30. <i>Organometallic polymerisation catalysts</i>					
30.1	C. Beermann and H. Bestian	<i>Angew. Chem.</i> 71 , 618 (1959)	Organometallic titanium compounds as polymerisation catalysts	6 (16)	
30.2	M. N. Berger, G. Boocock, and R. N. Howard	<i>Advan. Catal.</i> 19 , 211 (1969)	The polymerisation of olefins by Ziegler catalysts	30 (38)	
30.3	H. Bestian and K. Clauss	<i>Angew. Chem.</i> 75 , 1068 (1963); <i>Angew. Chem. Int. Ed. Engl.</i> 2 , 704 (1963)	Reactions of olefins with the titanium-carbon bond	11 (17)	
30.4	H. Bestian, K. Clauss, H. Jensen, and E. Prinz	<i>Angew. Chem.</i> 74 , 955 (1962); <i>Angew. Chem. Int. Ed. Engl.</i> 2 , 32 (1963)	Low temperature polymerisation of ethylene	10 (26)	

30.5	G. Bier	<i>Angew. Chem.</i> 73 , 186 (1961)	High molecular weight olefin mixed polymers prepared using mixed Ziegler catalysts	12 (35)	
30.6	N. M. Bikales	<i>Advan. Chem. Ser.</i> 70 , 233 (1968)	Homogeneous catalysis of polymerisation	17 (43)	
30.7	F. Dawans and P. Teyssié	<i>Bull. Soc. Chim. Fr.</i> 2376 (1963)	Mechanism of stereospecific polymerisation by transition metals	17 (222)	
30.8	G. Henrici-Olivé and S. Olivé	<i>Angew. Chem.</i> 79 , 764 (1967); <i>Angew. Chem. Int. Ed. Engl.</i> 6 , 790 (1967)	The active species in homogeneous Ziegler-Natta catalysts for the polymerisation of ethylene	9 (28)	
30.9	S. Inoue	<i>Nippon Kagaku Zasshi</i> 91 , 297 (1970)	Polymerisation by organometallic compounds		Japan.
30.10	E. B. Milovskaya, L. V. Zamoiskaya, and E. L. Kopp	<i>Usp. Khim.</i> 38 , 928 (1969); <i>Russ. Chem. Rev.</i> 38 , 420 (1969)	Mechanism of the initiation of radical polymerisation of polar monomers in systems comprising organometallic compounds	13 (135)	
30.11	G. Natta	<i>Makromol. Chem.</i> 35 , 94 (1960); <i>Usp. Khim.</i> 30 , 292 (1961)	Advances in stereospecific polymerisation	38 (37)	
30.12	G. Natta	<i>Pure Appl. Chem.</i> 12 , 165 (1966)	Some remarks on the mechanism of the stereospecific ionic coordinate polymerisation of hydrocarbon monomers	18 (60)	Main lecture, Int. Symp. Macromol. Chem., Prague, 1965
30.13	G. Natta, G. Dall'Asta, G. Mazzanti, U. Giannini, and S. Cesca	<i>Angew. Chem.</i> 71 , 205 (1959)	Stereospecific polymerisation of vinyl ethers	6 (18)	
30.14	F. Patat and H. Sinn	<i>Angew. Chem.</i> 70 , 496 (1958)	The result of low pressure polymerisation of α -olefins: polymerisation by complexes	5 (28)	

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Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
30. Organometallic polymerisation catalysts (cont'd)					
30.15	H. Sinn and F. Patat	<i>Angew. Chem.</i> 75 , 805 (1963); <i>Angew. Chem. Int. Ed. Engl.</i> 3 , 93 (1964)	The mechanism of action of organo-metallic catalysts	9 (18)	
30.16	J. K. Stille	<i>Chem. Rev.</i> 58 , 541 (1958)	Polymerisation of olefins by complex metal catalysts	40 (205)	
30.17	A. V. Topchiev, B. A. Krentsel', and L. L. Stotskaya	<i>Usp. Khim.</i> 30 , 462 (1961); <i>Russ. Chem. Rev.</i> 30 , 192 (1961)	Organometallic complexes: olefin polymerisation catalysts	16 (80)	Ziegler-type catalysts
See also: A32; A33					
31. Oxidative-addition and related reactions					
31.1	J. Chatt	<i>J. Inorg. Nucl. Chem.</i> 8 , 515 (1958)	Stabilisation of low-valent states of the transition metals	17 (52)	
31.2	J. P. Collman and W. R. Roper	<i>Advan. Organometal. Chem.</i> 7 , 53 (1968)	Oxidative-addition reactions of d ⁸ complexes	42 (125)	
31.3	J. P. Franck, C. Bocard, I. Serée de Roch, and L. Sajus	<i>Rev. Inst. Fr. Petrole Ann. Combust. Liquides</i> 24 , 710 (1969)	Molecular oxygen fixation by transition metal complexes: oxygen carriers	14 (61)	
31.4	J. Halpern	<i>Accounts Chem. Res.</i> 3 , 386 (1970)	Oxidative-addition reactions of transition metal complexes	7 (66)	
31.5	R. F. Heck	<i>Accounts Chem. Res.</i> 2 , 10 (1969)	Addition reactions of transition metal compounds	7 (36)	
31.6	K. Itoh and Y. Ishii	<i>Kagaku (Kyoto)</i> 24 , 420 (1969)	Addition-elimination reactions of organometallic compounds	14 (179)	Japan.
31.7	W. Kitching and C. W. Fong	<i>Organometal. Chem. Rev., Sect. A</i> 5 , 281 (1970)	Insertion of sulphur dioxide and sulphur trioxide into metal-carbon bonds	41 (77)	

31.8	L. Malatesta	<i>Endeavour</i> 28 , 30 (1969)	Zerovalent compounds of metals	5 (5)	
31.9	L. Malatesta, R. Ugo, and S. Cenini	<i>Advan. Chem. Ser.</i> 62 , 318 (1966)	Chemistry of zerovalent nickel, palladium and platinum derivatives	39 (209)	
31.10	O. M. Nefedov and M. N. Manakov	<i>Angew. Chem.</i> 78 , 1039 (1966); <i>Angew. Chem. Int. Ed. Engl.</i> 5 , 1021 (1966)	Inorganic, organometallic and organic analogues of carbenes	18 (185)	
31.11	S. Otsuka and Y. Tatsumo	<i>Yuki Gosei Kagaku Kyokai Shi</i> 28 , 902 (1970)	Interactions of sulphur dioxide with metal complexes	13	Japan.
31.12	R. Ugo	<i>Coord. Chem. Rev.</i> 3 , 319 (1968)	The coordinative reactivity of phosphine complexes of platinum(0), palladium(0) and nickel(0)	26 (82)	
31.13	L. Vaska	<i>Accounts Chem. Res.</i> 1 , 335 (1968)	Reversible activation of covalent molecules by transition metal complexes. The role of the covalent molecule	10 (51)	
31.14	G. Wilkinson	<i>Platinum Metals Rev.</i> 12 , 50 (1968)	Tertiary phosphine complexes of the platinum metals	4 (13)	Oxidative-addition reactions
31.15	T. Yoshino	<i>Kagaku No Ryoiki</i> 11 , 491 (1957)	Complexes in which the metal has an oxidation state of zero	9 (36)	Japan.
See also: 4.25; 15.17; 29.9					
32. <i>Ligand reactivity in complexes</i>					
32.1	J. P. Collman	<i>Transition Metal Chem.</i> 2 , 1 (1966)	Reactions of ligands coordinated with transition metals	114 (303)	
32.2	M. A. Haas	<i>Organometal. Chem. Rev., Sect. A</i> 4 , 307 (1969)	Reactivity of organo-transition metal complexes: proton addition and hydride abstraction reactions of the organic ligands	37 (170)	

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Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
32. <i>Ligand reactivity in complexes(cont'd)</i>					
32.3	W. Kitching	<i>Organometal. Chem. Rev.</i> 3, 61 (1968)	Some aspects of oxymetalation	74 (161)	Esp. pp. 124-129, palladium and platinum
32.4	W. Kitching	<i>Organometal. Chem. Rev.</i> 3, 35 (1968)	Recent aspects of the mercuration reaction	26 (72)	Esp. pp. 50-53, metallocenes, etc; 57-58, auration, palladation, and platination
32.5	A. K. Prokof'ev, V. I. Bregadze, and O. Y. Okhlobystin	<i>Usp. Khim.</i> 39, 412 (1970); <i>Russ. Chem. Rev.</i> 39, 196 (1970)	Intramolecular coordination in organo-metal (metalloid) compounds	32 (210)	
32.6	D. A. White	<i>Organometal. Chem. Rev.</i> 3, 497 (1968)	Electrophilic and nucleophilic attack on organo-transition metal compounds	58 (263)	
33. <i>Photochemistry</i>					
33.1	A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischner, and R. D. Lindholm	<i>Chem. Rev.</i> 68, 541 (1968)	Photochemistry of transition-metal coordination compounds	45 (472)	
33.2	E. Koerner von Gustorf and F.-W. Grevels	<i>Fortschr. Chem. Forsch.</i> 13, 366 (1969)	Photochemistry of metal carbonyls metallocenes and olefin complexes	85 (581)	
33.3	W. Strohmeier	<i>Angew. Chem.</i> 76, 873 (1964); <i>Angew. Chem. Int. Ed. Engl.</i> 3, 730 (1964)	Photochemical substitutions on metal carbonyls and their derivatives	8 (68)	

See also: A52

34. *Organometallic complexes of biological interest*

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| 34.1 | K. Bernhauer,
O. Müller, and
F. Wagner | <i>Angew. Chem.</i> 75 ,
1145 (1963);
<i>Angew. Chem. Int.</i>
<i>Ed. Engl.</i> 3 , 200
(1964) | New chemical and biochemical
developments in the vitamin B ₁₂
field | 12
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| 34.2 | R. Bonnett | <i>Chem. Rev.</i> 63 , 573
(1963) | The chemistry of the vitamin B ₁₂
group | 33
(293) | |
| 34.3 | A. Eschenmoser | <i>Pure Appl. Chem.</i>
20 , 1 (1969) | The role of transition metals in the
chemical synthesis of corrins | 23
(22) | Plenary lecture, 8ICCC |
| 34.4 | G. N. Schrauzer | <i>Accounts Chem. Res.</i>
1 , 97 (1968) | Organocobalt chemistry of vitamin
B ₁₂ model compounds (cobal-
oximes) | 7
(40) | |
| 34.5 | I. Ugi | <i>Record Chem. Progr.</i>
30 , 289 (1969) | A novel synthetic approach to pep-
tides by computer planned stereo-
selective four-component con-
densations of α -ferrocenylalkyl-
amines and related reactions | 23
(30) | |

35. *Electronic structures of organometallic complexes*

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| 35.1 | D. A. Brown | <i>Roy. Inst. Chem. J.</i>
88 , 65 (1964) | Bond theory of organometallic
compounds | 6
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| 35.2 | D. A. Brown | <i>Transition Metal</i>
<i>Chem.</i> 3 , 1 (1966) | Electronic structures of some
organometallic molecules | 55
(150) |
| 35.3 | D. A. Brown | <i>Record. Chem. Progr.</i>
30 , 211 (1969) | The bond theory of organometallic
compounds | 12
(21) |
| 35.4 | J. W. Cable and
R. K. Sheline | <i>Chem. Rev.</i> 56 , 1
(1956) | Bond hybridisation and structure
in the metal carbonyls | 26
(91) |
| 35.5 | M. E. Dyatkina | <i>Usp. Khim.</i> 27 , 57
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in aromatic complexes of metals | 37
(83) |
| 35.6 | J. C. Kotz and
D. G. Pedott | <i>Organometal. Chem.</i>
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(115) |

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35. <i>Electronic structures of organometallic complexes (cont'd)</i>					
35.7	J. Kragten	<i>Chem. Weekbl.</i> 54 , 337, 349 (1958)	Electronic configuration of ferrocene and analogous compounds	8 + 4 (28)	Dutch
35.8	E. Lindner	<i>Angew. Chem.</i> 82 , 143 (1970); <i>Angew. Chem. Int. Ed. Engl.</i> 9 , 114 (1970)	The behaviour of acid halides towards Lewis acids and Lewis bases	10 (83)	
35.9	F. D. Mango	<i>Advan. Catal.</i> 20 , 291 (1969)	Molecular orbital symmetry conservation in transition metal catalysis	35 (43)	
35.10	E. L. Muetterties and R. A. Schunn	<i>Quart. Rev.</i> 20 , 245 (1966)	Pentacoordination	55 (316)	
35.11	D. F. Shriver	<i>Accounts Chem. Res.</i> 3 , 231 (1970)	Transition metal basicity	8 (68)	
35.12	S. Yamada	<i>Kogyo Kagaku Zasshi</i> 60 , 1343 (1957)	Chemical bonds in organometallic compounds	9 (81)	Japan.
See also: A38.1; E5.3; E10; 11.3					
36. <i>Physical methods—infrared spectroscopy</i>					
36.1	H. P. Fritz	<i>Advan. Organometal. Chem.</i> 1 , 240 (1964)	Infrared and Raman spectral studies of π -complexes formed between metals and C_6H_6 rings	77 (180)	
36.2	L. M. Haines and M. H. B. Striddard	<i>Advan. Inorg. Chem. Radiochem.</i> 12 , 53 (1969)	Vibrational spectra of transition metal carbonyl complexes	81 (340)	
36.3	R. E. Hester	<i>Coord. Chem. Rev.</i> 2 , 319 (1967)	Raman spectroscopic studies in coordination chemistry	29 (204)	Esp. pp. 338–343
36.4	D. K. Huggins and H. D. Kaesz	<i>Progr. Solid State Chem.</i> 1 , 417 (1964)	Use of infrared and Raman spectroscopy in the study of organometallic compounds	95 (326)	

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| 36.5 | E. König,
H. L. Schlofer, and
S. Herzog | <i>Z. Chem.</i> 4 , 95 (1964) | Techniques for absorption and reflection spectroscopy with extremely oxygen-sensitive compounds | 6
(21) | |
| 36.6 | T. G. Spiro | <i>Progr. Inorg. Chem.</i> 11 , 1 (1970) | Vibrational spectra and metal-metal bonds | 51
(145) | |
| 36.7 | D. W. James and
M. J. Nolan | <i>Progr. Inorg. Chem.</i> 9 , 195 (1968) | Vibrational spectra of transition metal complexes and the nature of the metal-ligand bond | 81
(198) | Metal-carbon bonds, pp. 261-265 |
- See also: A40.3; A47.1; A56; 11.13
37. *Physical methods—nuclear magnetic resonance*
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| 37.1 | H. J. Keller and
K. E. Schwarzhans | <i>Angew. Chem.</i> 82 , 227 (1970); <i>Angew. Chem. Int. Ed. Engl.</i> 9 , 196 (1970) | Magnetic resonance of paramagnetic complex compounds | 10
(67) | |
| 37.2 | M. L. Maddox,
S. L. Stafford, and
H. D. Kaesz | <i>Advan. Organometal. Chem.</i> 3 , 1 (1965) | Applications of nuclear magnetic resonance to the study of organometallic compounds | 179
(380) | |
| 37.3 | K. Vrieze,
H. C. Volger, and
P. W. N. M. van
Leeuwen | <i>Inorg. Chim. Acta Rev.</i> 3 , 109 (1969) | Reactions involving organometallic compounds of rhodium, iridium, palladium and platinum: a survey of NMR studies | 20
(77) | |
- See also: A40.8; A40.10; A57.2; 20.1
38. *Physical methods—mass spectrometry*
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| 38.1 | M. I. Bruce | <i>Advan. Organometal. Chem.</i> 6 , 273 (1968) | Mass spectra of organometallic compounds | 61
(255) | |
| 38.2 | M. Cais and
M. S. Lupin | <i>Advan. Organometal. Chem.</i> 8 , 211 (1970) | Mass spectra of metallocenes and related compounds | 123
(201) | |
| 38.3 | D. B. Chambers,
F. Glockling, and
J. R. C. Light | <i>Quart. Rev.</i> 22 , 317 (1968); <i>Usp. Khim.</i> 38 , 1294 (1969) | Mass spectra of organometallic compounds | 21
(51) | |

(Continued)

Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
38. <i>Physical methods—mass spectrometry (cont'd)</i>					
38.4	J. Lewis and B. F. G. Johnson See also: A40.4; B6.2	<i>Accounts Chem. Res.</i> 1 , 245 (1968)	Mass spectra of some organometallic molecules	12 (35)	
39. <i>Physical methods—miscellaneous</i>					
39.1	V. I. Gol'danskii, V. V. Khrapov, and R. A. Stukan	<i>Organometal. Chem. Rev., Sect. A</i> 4 , 225 (1969)	Application of the Mössbauer effect in the study of organometallic compounds	37 (129)	Organoiron complexes
39.2	A. D. Garnovskii, O. S. Osipov, and V. I. Minkin	<i>Usp. Khim.</i> 37 , 1782 (1968); <i>Russ. Chem. Rev.</i> 37 , 763 (1968)	Dipole moments and the structure of π -complexes of metals	17 (298)	
39.3	S. P. Gubin	<i>Pure Appl. Chem.</i> 23 , 463 (1970)	Application of electrochemical methods in the organometallic chemistry of transition metal π -complexes	25 (55)	Section lecture, 4 ICOMC
See also: A40.6; A40.7; A40.9					
40. <i>Structural studies</i>					
40.1	M. R. Churchill	<i>Trans. N.Y. Acad. Sci.</i> 31 , 280 (1969)	Structural information on the bonding in some organo-transition metal complexes	10 (25)	
40.2	M. R. Churchill and R. Mason	<i>Advan. Organometal. Chem.</i> 5 , 93 (1967)	The structural chemistry of organo-transition metal complexes: some recent developments	43 (159)	
40.3	A. I. Gusev and Y. T. Struchkov	<i>Zh. Strukt. Khim.</i> 11 , 368 (1970)	Structure of π -olefinic and π -acetylenic complexes of transition metals	33 (114)	To 1969

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| 40.4 | G. A. Kukina | <i>Zh. Strukt. Khim.</i> 3 ,
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(87) | Japan. |

See also: A40.5; A57.1; 11.2; 11.11; 23.2

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| 41.1 | W. F. Lautsch,
A. Tröber,
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41.2	W. Lautsch, A. Tröber, H. Körner, K. Wagner, R. Kaden, and S. Blase	<i>Z. Chem.</i> 4 , 441 (1964)	Energetic data for metalorganic compounds 2. Enthalpies of vaporisation and formation	14 (155)	
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42.1	A. D. Allen and F. Bottomley	<i>Accounts Chem. Res.</i> 1 , 360 (1968)	Inorganic nitrogen fixation. Nitrogen compounds of the transition metals	6 (40)	
42.2	Y. G. Borod'ko and A. E. Shilov	<i>Usp. Khim.</i> 38 , 761 (1969); <i>Russ. Chem. Rev.</i> 38 , 355 (1969)	Complexes of molecular nitrogen	20 (121)	
42.3	F. Bottomley	<i>Quart. Rev.</i> 24 , 617 (1970)	The reactions of hydrazine with transition-metal complexes	22 (132)	
42.4	W. Büttner	<i>Z. Chem.</i> 9 , 219 (1969)	Chemical activation of molecular nitrogen by transition metal complexes	9 (61)	

42.5	J. Chatt	<i>Platinum Metals Rev.</i> 13 , 9 (1969)	Nitrogen complexes of the platinum metals. Pointers to a mechanism of fixation	6 (20)	
42.6	J. E. Fergusson and J. L. Love	<i>Rev. Pure Appl. Chem.</i> 20 , 33 (1970)	A survey of dinitrogen complexes of the transition metals	18 (93)	
42.7	P. C. Ford	<i>Coord. Chem. Rev.</i> 5 , 75 (1970)	Properties and reactions of ruthenium(II) amine complexes	25 (67)	Includes nitrogen complexes
42.8	P. F. Fottrell	<i>Sci. Progr.</i> 56 , 541 (1968)	Recent advances in biological nitrogen fixation	15	
42.9	G. Henrici-Olivé and S. Olivé	<i>Angew. Chem.</i> 81 , 679 (1969); <i>Angew. Chem. Int. Ed. Engl.</i> 8 , 650 (1969)	Non-enzymatic fixation of nitrogen	10 (47)	
42.10	T. Ho and A. Yamamoto	<i>Yuki Gosei Kagaku Kyokai Shi</i> 28 , 598 (1970)	Recent studies on nitrogen fixation by transition metal complexes	21	Japan.
42.11	K. Kuchynka	<i>Catal. Rev.</i> 3 , 111 (1969)	Fixation of molecular nitrogen	33 (78)	
42.12	J. C. Marchon	<i>Sci. Progr. Decouverte No.</i> 3420 , 15 (1970)	Fixation of atmospheric nitrogen: a new way	6 (15)	
42.13	G. Martino and L. Sajus	<i>Rev. Inst. Fr. Petrole Ann. Combust. Liquides</i> 25 , 36 (1970)	Activation of nitrogen by transition metal complexes	20 (115)	
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42.15	L. E. Mortensen	<i>Survey Progr. Chem.</i> 4 , 127 (1968)	Nitrogen fixation	37 (54)	A biochemical view
42.16	R. Murray and D. C. Smith	<i>Coord. Chem. Rev.</i> 3 , 429 (1968)	The activation of molecular nitrogen	42 (172)	
42.17	Y. Uchida and M. Hidai	<i>Bussei</i> 8 , 265 (1968)	Activation of molecular nitrogen by transition metal complexes	8	Japan.

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Ref. No.	Authors	Reference	Title	No. of pages (No. of ref.)	Comments
42. <i>Molecular nitrogen (dinitrogen) complexes (cont'd)</i>					
42.18	E. E. van Tamelen	<i>Accounts Chem. Res.</i> 3 , 361 (1970)	Design and development of an organic-inorganic system for the chemical modification of molecular nitrogen under mild conditions	7 (25)	
42.19	M. E. Vol'pin and V. B. Shur	<i>Zh. Vses. Khim. Obshch.</i> 12 , 31 (1967)	Complex formation as a means for activation of molecular nitrogen	11 (43)	Russ.
43. <i>Other topics of related interest</i>					
43.1	M. J. Cleare	<i>Platinum Metals Rev.</i> 12 , 131 (1968)	Nitrosyl complexes of the platinum metals	3 (18)	
43.2	W. P. Griffith	<i>Advan. Organometal. Chem.</i> 7 , 211 (1968)	Organometallic nitrosyls	29 (99)	
43.3	B. F. G. Johnson and J. A. McCleverty	<i>Progr. Inorg. Chem.</i> 7 , 277 (1966)	Nitric oxide complexes of transition metals	83 (264)	
43.4	J. Lewis	<i>Sci. Progr.</i> 47 , 506 (1959)	Recent advances in science: inorganic chemistry	16 (43)	Nitrosyl compounds
43.5	J. Lewis	<i>Record Chem. Progr.</i> 22 , 147 (1961)	Coordination complexes involving nickel and nitric oxide	9 (11)	
43.6	L. Malatesta	<i>Progr. Inorg. Chem.</i> 1 , 283 (1959)	Isocyanide complexes of metals	97 (117)	Later expanded into book
43.7	J. Mašek	<i>Inorg. Chim. Acta Rev.</i> 3 , 99 (1969)	Electrophilic reactivity and structure of coordinated nitrosyl groups	10 (36)	
See also: A37.2					

Ligand Substitution in Transition Metal π -Complexes

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I. Introduction	347
II. General Comments on Ligand Substitution in Complexes	348
III. π -Complexes with Ligands Stable in a Noncoordinated State	352
A. Acetylene Complexes	352
B. Olefin Substitution Reactions	355
C. π -Arene-Transition Metal Complexes	365
IV. π -Complexes with Ligands Unstable in a Noncoordinated State	371
A. π -Allyl Substitution and Transfer Reactions	371
B. Transfer of the π -Tetraphenylcyclobutadienyl Ligand	378
C. Substitution and Transfer of the π -Cyclopentadienyl Ligand	383
V. Conclusion	409
References	409

I

INTRODUCTION

Ligand substitution is one of the most characteristic reactions of coordination compounds. If in the early stages of the development of coordination chemistry a ligand substitution reaction served as a synthetic method, then later on, especially after Werner, such reactions were widely employed both to solve structural problems (viz., geometric isomerism), and to elucidate the nature of a trans effect.

Although quantitative studies of substitution reactions have only been launched quite recently, a considerable body of experimental data is available, so that theoretical principles of ligand substitution mechanisms in classical inorganic complexes have been developed. Unfortunately the same cannot be said for substitution reactions involving π -bonded hydrocarbon ligands, in spite of a continuously expanding number of publications in this field. In the majority of studies substitution reactions are used to obtain novel transition metal π -complexes, and a far lesser number of papers deal with the quantitative aspects of the exchange.

Information on ligand substitution mechanisms should aid us to understand more profoundly homogeneous catalysis by transition metal complexes, where probably consecutive substitution and transfer reactions of ligands from metal to a substrate and back take place continuously.

This review summarizes experimental results on the substitution and transfer reactions¹ of hydrocarbon ligands in transition metal π -complexes. Moreover, an attempt is also made to discuss these results in terms of ligand substitution in complexes in general.

II

GENERAL COMMENTS ON LIGAND SUBSTITUTION IN COMPLEXES

The kinetics and mechanisms of substitution reactions studied in detail have been reviewed elsewhere (1-3). Here we shall summarize some recent data obtained in this field. As far as terminology is concerned, in the majority of cases that of Ingold (4) has been used, in which substitution of one ligand by another is regarded as a nucleophilic (SN) reaction. However, such a classification is rather rigid, and the term "nucleophilicity" is imprecise if one considers the variety of ligands from the simplest anions to olefins, acetylenes, arenes, etc.

Also, ligand substitution may occur as an electrophilic process. The presence of electrons in nonbonding or antibonding molecular orbitals of the substrate, and the ability of an attacking agent to withdraw such electrons (to vacant orbitals), are the structural factors favoring electrophilic substitution of ligands. Moreover it is rather difficult to assign some substitution reactions to one or other of the two main classes. Thus Langford and Gray's classification (3) of ligand substitution is also worthy of attention. It is based on the nature of the transition state instead of the nature of the attacking reagent. According to these authors three mechanisms may operate for ligand substitution in complexes: the first is a dissociative (so-called D-type) mechanism in which formation of an intermediate having a decreased coordination number is a rate-determining step. It is obvious that it corresponds to the SN₁ mechanism of Ingold and Hughes.

¹ We shall distinguish two types of reactions: substitution of one ligand by another $ML_n + L' \rightarrow ML_{n-1}L' + L$, and a ligand transfer from one metal to another $ML_n + M'L'_m \rightarrow ML_{n-1} + M'L'_mL$.

A second mechanism involves a transition state in which the metal forms weak bonds between the group to be substituted and the entering ligand, i.e., and associative A-type mechanism (SN_2 reaction in the Ingold classification). Finally a third possibility is suggested in which an intermediate complex cannot be detected from the kinetics. Langford and Gray denote this mechanism by I. Two limiting cases are distinguished, depending upon the factors determining the reaction rate: dissociative activation (I_d) when the reaction is defined generally by the nature of the leaving group, and associative activation (I_a) in which the rate of the substitution reaction is determined equally (or to a great extent) by the nature of the entering ligand. It can be seen that both I_a and I_d are intermediate mechanisms, and in that sense do not fall into the Ingold and Hughes classification. In the discussion that follows Langford and Gray's terminology is used.

In accord with these mechanisms, in the course of substitution, intermediates or transition states with unusual coordination numbers and geometries can be found. They are usually different from those of the ground state for the complex under study. For example, in the octahedral complexes ligand substitution involves a transition state with coordination number equal to 7. Moreover, in the D-type mechanism two geometric isomers involving a five-coordinate intermediate can be found: viz., a trigonal bipyramid or a square pyramid. The latter is stabilized more by the ligand field whereas the former is more likely when bulky groups are involved, or in the presence of ligands capable of producing strong π -bonds with the metal. Transition states with coordination number equal to 5 may also arise in the A-substitution mechanism for square-planar complexes. More detailed information on five-coordinate transition states can be found in Nyholm and Tobe's review (5). Three-coordinate transition metal intermediates are rather rare but are theoretically possible for D-type substitution in tetragonal and tetrahedral complexes.

Thus the ability of the metal to change both its geometric configuration and its coordination number in the transition state is an important condition in ligand substitution reactions. The experimental data available on ligand substitution in inorganic complexes lead to a most significant conclusion: namely, that the possibility of reacting by one or the other mechanism is determined essentially by the coordination numbers of the starting complexes. For example, octahedral complexes usually react by a D-type mechanism, whereas square-planar compounds always follow an A-type substitution mechanism. Exceptions are defined either by a specificity of

the entering ligand [thus ligands capable of forming strong π -bonds may favor A substitution in octahedral complexes (3)] or by the nature of the central atom. It is common knowledge that in a series of six-coordinate chromium, molybdenum, and tungsten complexes the ability to react by the A-type mechanism increases with increasing size of the central metal atom. (6). The nature of the solvent is another factor which effects mechanisms of substitution (7). Almost all ligand substitution reactions of inorganic transition metal complexes have been studied in aqueous media. Usually, under these conditions ligand substitution is preceded either by hydrolysis or by aquation. Hydrogen bond formation, participation of water and its conjugated base, OH ion, in the acid-base equilibria, the polar properties of water, etc., are all factors which determine the observed reaction kinetics.

In contrast, ligand substitution reactions of transition metal π -complexes usually occur in organic media in which side processes are less significant, and the kinetics are therefore simpler.

All the π -bonded hydrocarbon ligands (apart from the ethylenic and acetylenic ones²) are polydentate. At present it is commonly held that the π -cyclopentadienyl and arene ligands occupy three coordination sites, and π -allyl and cyclobutadienyl ones two sites.

It is generally thought that on substitution, polydentate ligands (e.g., ethylenediamine) are capable of successive cleaving of each metal-ligand bond without any considerable influence of one coordinating group on the properties of the other, and without any change in electron density distribution in the ligand (8). This concept evidently makes sense only for substitution involving nonconjugated olefins. In all other cases such substitution (specifically for ligands with delocalized π -bonds) would affect the nature of the metal-ligand bond and the electron density distribution in the ligand. Naturally such a process requires larger energy.

Therefore, it can be assumed that D-type substitution of polydentate π -ligands is least probable. The A-type mechanism is most probable for square-planar complexes. However, for compounds with coordination number 6 and larger an association with an entering ligand will imply transition states of higher coordination numbers (account should also be taken that the entering ligand might in turn be a polydentate group). Thus in this case in the transition state, metal- π -ligand "old" bonds would

² Sometimes, for example, a bridging acetylene ligand may occupy two coordination sites but not on the same metal atom.

partially cleave and require, as noted above, the higher energy. i.e., more rigorous conditions. This course of substitution in π -complexes involving polydentate hydrocarbon ligands (cyclopentadienyl, cycloheptatriene, arene, etc.) seems most probable, since coordination with an entering ligand usually capable of strong π -bond formation may stabilize a transition state having partially cleaved "old" metal- π -ligand bonds. Moreover, a strong trans effect of the entering ligand should assist in partial breakdown of a metal-leaving ligand bond in the transition state. However, when coordination with the entering ligand does not partially cleave the "old" bonds (in the square-planar or tetrahedral complexes), the trans effect of the new ligand will try to change the character of the remaining π -ligand-metal bond. If the latter undergoes such changes rather readily, then one may suggest that π -bonded ligands rearrange into ligands having some intermediate type of bonding (in the limiting case to σ -bonded ligands) prior to substitution.

For substitution of monodentate π -hydrocarbon ligands (ethylene, acetylene) *a priori* both mechanisms are possible. In this case an ability to change the coordination number in the transition state will be decisive. It is probable that square-planar complexes react by an associative mechanism with an increase in coordination number in the transition state. For the octahedral complexes, intermediates with lower coordination number are preferable (D-type mechanism). There is as yet no evidence for a transition state involving σ -bonded ethylene or acetylene.³ However, both molecules are capable of inserting into transition metal-carbon σ -bonds (10). It is quite probable that such an insertion mechanism operates in the Ziegler-Natta ethylene polymerization (11).

Thus it is quite probable that the general features determined by stereochemistry are again valid in passing from classical complexes to those with π -bonded hydrocarbon ligands. Ability to engage in back-donation may explain the high tendency of those complexes to react by an associative mechanism.

Depending upon the nature of the ligand to be substituted, all π -complexes known can be divided conveniently into two classes:

(1) compounds with ligands stable in a noncoordinated state (olefins, acetylenes, and aromatics such as benzene);

³ See, however, Kaplan *et al.* (9).

(2) compounds with ligands unable to exist in a noncoordinated form (allyl, cyclobutadienyl, and cyclopentadienyl)

The compounds of the first group are more suitable for physicochemical investigation (isotopic substitution, study of substituent effects, spectral methods, etc.) so reactions involving these complexes have been studied in more detail and sometimes quantitatively.

Exchange reactions in the second group of complexes are more difficult to investigate because the ligands do not exist in solution as individual molecules.

III

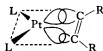
π -COMPLEXES WITH LIGANDS STABLE IN A NONCOORDINATED STATE

A. Acetylene Complexes

The structure of transition metal-acetylene complexes has been discussed in detail by Bennett (12) and in Temkin and Flid's monograph (13). Substitution reactions of acetylene ligands have been reported mainly for platinum complexes. Platinum(II) forms the following types of acetylenic complex: $[\text{PtCl}_2(\text{RC}\equiv\text{CR})(\text{amine})]$, $\text{M}[\text{PtCl}_3(\text{RC}\equiv\text{CR})]$, and $[\text{PtCl}_2(\text{RC}\equiv\text{CR})]_2$, the structures of which are analogous to those of the respective ethylenic compounds (14). There is as yet no final solution to the problem of bonding in acetylenic Pt(0) derivatives $\text{L}_2\text{Pt}(\text{RC}\equiv\text{CR})$. Two structures have been proposed by Chatt *et al.* (15).



(I)



(II)

In structure (I) the platinum has effectively a coordination number of 3 with the alkyne occupying one coordination site, while in (II), with a coordination number for platinum of 4, acetylene behaves as a bidentate ligand. Preliminary X-ray data for $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{Ph}_2)$ (16) favor structure (II) but do not completely eliminate structure (I). Bond character in Pt-acetylene complexes has also been discussed (17).

In these complexes the acetylene ligand can be readily substituted by some other ligands. The following general order of stability has been established (15).



R = alkyl

Relatively high stability in ligand substitution reactions is associated with the rather high ability of platinum to form retrodative bonds. Thus the acetylene is a π -acceptor and should therefore facilitate the trans-ligand A-type substitution (1). This has been confirmed by the data of Allen and Theophanides (18) on the hydrolysis of $\text{K}[(\text{acetylene})\text{PtCl}_3]$.

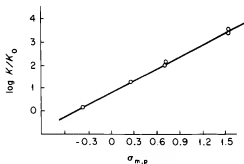
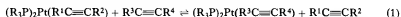


FIG. 1. $\log K/K_0$ vs. $\sigma_{(X)}$ for the exchange reaction of the complexes $(\text{R}_3\text{P})_2\text{Pt}(\text{HC}\equiv\text{CC}_6\text{H}_4\text{X})$ [from Temkin and Flid (13)].

With a strong trans donor (for example, PPh_3)⁴ one should expect D-type substitution of the acetylenic ligand to take place; evidence for this is obtained from the kinetic data of the reaction

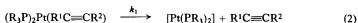


It has been found (20) that the reaction rate is independent of both the nature and concentration of the attacking agent. Dependence of the equilibrium constants upon the character of the substituents in the acetylene obeys the Hammett (21) equation $\log K/K_0 = \rho\sigma$, where K and K_0 are the equilibrium constants of the substituted and unsubstituted phenylacetylenes, respectively (Fig. 1).

⁴ With respect to platinum group metals, the phosphorus ligands behave as strong σ -donors rather than π -acceptors (cf. 19).

The electron-attractive effect of the substituents shifts the equilibrium to the side of the reactants [Eq. (1)]. The first-order rate constant decreases in the same direction. Since stability of the complexes is defined by the same factors, Pt-acetylene bond cleavage is probably the rate-determining step. The effects of phenyl ring substituents in triphenylphosphine on the reaction rate have also been studied (20). Electron-releasing substituents slow down the reaction and behave analogously to the electronegative ones in the acetylenic part of the molecule.

These results are interpreted in terms of a dissociative mechanism. The decay of the complex proceeds according to the following scheme as a limiting step (21):

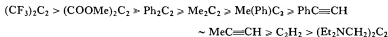


The reverse reaction is determined by the nature of R. The generating $[Pt(PR_3)_2]$ moiety is a rather stable intermediate. A comparison of the results obtained with the NMR data (22) of substituted phenylacetylenes led to the conclusion that there is a relation between equilibrium constant, first-order rate constants, and chemical shifts of the acetylenic proton: they all depend on substituent effects on the electron density in the triple bond.

Acetylene substitution has also been investigated for cobalt complexes, $Co_2(CO)_6(C_2RR^1)$ (23). Based on the X-ray study three possible structures have been proposed (24). It was found that the $C\equiv C$ bond length in the alkyne is equal to 1.46 Å, and the $C\equiv C-H$ angles approach 120° . Thus, owing to coordination, the acetylene molecule geometry resembles that of an olefinic ligand. However, substitution of the bridged acetylenic ligands obeys the kinetics of the exchange reaction in the Pt(0) complexes (23) discussed above. The constants for the equilibrium



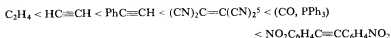
essentially depend on the nature of the substituent. The following order of reactivity has been observed:



i.e., stability increases markedly with substituent electronegativity. It is interesting that by replacing the CO in $Co_2(CO)_6(C_2RR^1)$ one observes a reverse dependence (25). This is in conformity with an increase in Co—Co

bond strength, which is confirmed by a corresponding decrease of $\nu(\text{CO})$. At the same time the activation parameters of the substitution reaction for both the carbonyl and alkyne ligands are similar, and characterize a dissociative-type process. It has been assumed (23) that both reactions proceed by a D-type mechanism. Cleavage of the cobalt-acetylene bond is the limiting step.

Thus all the data on acetylene substitution are interpreted in terms of a dissociative mechanism with metal-ligand bond cleavage as a limiting step of the reaction. Based on experimental data on replacement of one ligand by another ligand the following sequence of ligand substitution is established.



in which each successive ligand replaces any foregoing one. Except for ethylene, all these ligands react via a dissociative substitution in spite of the fact that they produce more stable complexes than ethylene does (27-29).

B. Olefin Substitution Reactions

This section is concerned in part with substitution of mono-, di-, and polyolefins in some transition metal π -complexes. Structures of these compounds and methods of synthesis have been discussed in detail by Bennett (12), Hartley (30), and other authors (31). Dewar's (32) concept of bonding advanced for silver-olefin complexes and extended by Chatt (33) to the platinum ones is commonly accepted at present. It is assumed that bond formation is the result of an overlap between the vacant metal orbitals and the occupied π -olefin orbitals (a bond of σ -symmetry), coupled with an overlap of a filled metal orbital and an antibonding π^* -ligand orbital (a π -bond). Such an interpretation is in a good agreement with the X-ray data for Zeise's salt (34), with the monoolefin molecule occupying one coordination site and arranged perpendicularly to the ClPtCl plane. Quantitative data on bond strengths have been reported for silver complexes. From dissociation constants the estimated enthalpy change for the reaction (35)



⁵ See Baddley and Venanzi (26).

is about 6 kcal, which suggests a silver-olefin bond energy of about 30 kcal. Another criterion of metal-olefin bond strength is the decrease in the C=C bond stretching frequency on coordination. The bond is assumed to be stronger with a larger change in $\nu(\text{C}=\text{C})$ frequency. In this context and in the light of some chemical data, platinum complexes [where $\Delta\nu(\text{C}=\text{C})$ is about 150 cm^{-1}] are considered to be more stable than their silver analogs [where $\Delta\nu(\text{C}=\text{C})$ is about 50 cm^{-1}]⁶.

All known examples of studies on olefin substitution can be divided into two groups:⁷

(a) *Olefin substitution as a synthetic method.* These studies are usually least concerned with reaction mechanism. At best only a stability order for some particular types of complex has been determined. Table I lists examples of such reactions and does not involve replacement of other ligands by olefins. A more detailed discussion of such reactions can be found in Fischer and Herberhold's review (67).

(b) *Quantitative investigation of olefin substitution reactions.* A far smaller number of papers is concerned with this subject. The first qualitative results were obtained in 1936 by Anderson (68) who established a stability order for complexes in exchange reactions with other olefins: ethylene > styrene > amylene > cyclohexene > 1,1-diphenylethylene \geq 1,1-methylphenylethylene. Later Orchin *et al.* (69) found that a (*cis*-4-methyl-2-pentene)platinum complex has a stability which exceeds twice that of its *trans* isomer, and is much higher than that of the *cis*-pentene complex. In our opinion these results might be explained by steric shielding of the antibonding π^* -orbitals, thereby hindering formation of a strong retrodative bond. The effect of electronic factors on the stability of substituted styrene-platinum complexes has been discussed in detail by Orchin *et al.* (70-72). For the equilibrium



it has been shown (70) that 1-dodecene produces a more stable complex than any of the styrenes studied. All substituents X, independent of their nature, stabilize the styrene complex. A plot of equilibrium constants versus the σ -constants of the substituents gives a U-shaped curve with a minimum K

⁶ However, in other work (35a), $\nu(\text{C}=\text{C})$ decreases by about $300\text{--}400\text{ cm}^{-1}$ on coordination.

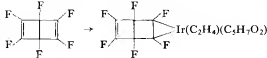


⁷ Use of the olefin substitution reaction for separating ethylene from propylene is discussed by Bock and Monerjan (36). Substitution reactions as a model for investigating the mechanism of homogeneous catalysis are considered by Baddley and Fraser (37).

TABLE I
SUBSTITUTION REACTIONS OF π -OLEFIN LIGANDS

Reaction	Reaction conditions ^a	% Yield	References
$(\pi\text{-C}_2\text{H}_4\text{PtCl}_2)_2 + \text{R}-\triangle \rightarrow \text{C}_2\text{H}_4 + (\text{R}-\triangle\text{PtCl})_n$	Benzene, 25°	—	38
$(\text{Ph}_3\text{P})_2\text{Ni}(\pi\text{-C}_2\text{H}_4) + \text{CF}_2=\text{CXY} \rightarrow \text{C}_2\text{H}_4 + (\text{Ph}_3)_2\text{Ni}(\text{CF}=\text{CXY})$ X, Y = Cl, Br, F	Ether, 25°, 12 hr	60–90	39
$\text{K}[\text{PtCl}_3(\pi\text{-C}_2\text{H}_4)] + \text{CO} \rightarrow \text{K}[\text{Pt}(\text{CO})\text{Cl}_3] + \text{C}_2\text{H}_4$	Acetone, 25°	—	40
$\text{Pt}(\pi\text{-C}_2\text{H}_4)(\text{Ph}_3\text{P})_2 + \text{C}_6\text{H}_4(\text{COO}^-)(\text{N}_2^+) \rightarrow \text{C}_6\text{H}_4(\text{COO})(\text{N}=\text{N})\text{Pt}(\text{PPh}_3)_2 + \text{C}_2\text{H}_4$	Benzene, 25°	Quant.	41
$(\text{Ph}_3\text{P})_2\text{Pt}(\pi\text{-C}_2\text{H}_4) + \text{C}_6\text{H}_4(\text{SO}_2)(\text{N}=\text{N}) \rightarrow \text{C}_6\text{H}_4(\text{SO}_2)(\text{N}=\text{N})\text{Pt}(\text{PPh}_3)_2 + \text{C}_2\text{H}_4$	Benzene, 10 min, -10°	Quant.	41
$(\pi\text{-C}_2\text{H}_4\text{PdCl}_2)_2 + \triangle \rightarrow \text{C}_2\text{H}_4 + (\pi\text{-ClC}_2\text{H}_4\text{C}_2\text{H}_4\text{PdCl})_2$	CH_2Cl_2 , 25°	—	42
$(\pi\text{-C}_2\text{H}_4)\text{PdCl}_2(p\text{-XC}_5\text{H}_4\text{N} \rightarrow \text{O}) + \text{PPh}_3 \rightarrow \text{C}_2\text{H}_4 + \text{Cl}_2\text{Pd}(\pi\text{-XC}_5\text{H}_4\text{N} \rightarrow \text{O})(\text{PPh}_3)$	CH_2Cl_2 , 25°	94	43
$(\pi\text{-C}_2\text{H}_4\text{PdCl}_2)_2 + \text{PhCH}=\text{CH}_2 \rightarrow [\text{Cl}_2\text{Pd}(\text{Ph}-\text{CH}=\text{CH}_2)]_2 + \text{C}_2\text{H}_4$	Benzene, 25°	40	44
$(\text{PhCH}=\text{CHPh})\text{PtCl}_2 + \text{C}_5\text{H}_5\text{N} \rightarrow (\text{C}_5\text{H}_5\text{N})_2\cdot\text{PtCl}_2 + \text{PhCH}=\text{CHPh}$	CHCl_3 , 25°	Quant.	45
$(\text{C}_5\text{H}_7\text{O}_2)\text{Rh}(\pi\text{-C}_2\text{H}_4)_2 + \text{Me}_2\text{C}=\text{C}=\text{CMe}_2 \rightarrow (\text{C}_5\text{H}_7\text{O}_2)\text{Rh}(\text{Me}_2\text{C}=\text{C}=\text{CMe}_2)_2$	—	—	46

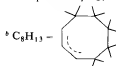
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TABLE I (continued)

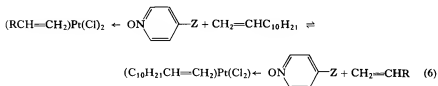
Reaction	Reaction conditions ^a	% Yield	References
$(C_5H_7O_2)Ir(\pi-C_2H_4)_2 + $  $\rightarrow (C_5H_7O_2)Ir(C_2H_4)(C_5H_7O_2)$	Ether, 25°, 12 hr	8	47
$[CIRh(\pi-C_2H_4)_2]_2 + PF_3 \rightarrow C_2H_4 + [(PF_3)_2RhCl]_2$	60°	Quant.	48
$[(\pi-RCH=CH_2)PtCl_2]_2 + 2,4,6-Me_3C_5H_2N \rightarrow$ $(2,4,6-Me_3C_5H_2N)_2PtCl_2 + C_2H_4$	—	—	49
$K[PtCl_3(\pi-C_2H_4)] + dipy \rightarrow (dipy)_2PtCl_2 + C_2H_4$	—	—	50
$(\pi-C_2H_4PtCl_2)_2 + PhC\equiv CSiMe_3 \rightarrow Me_3SiCl + C_2H_4 + (ClPtC\equiv CPh)_n$	Benzene, 25°	—	51
$(\pi-C_2H_4)AuCl + C_5H_6 \xrightarrow{Ph_3P} C_5H_5AuPPh_3 + C_2H_4$	THF	—	52
$(\pi-1,5-C_8H_{12})_2Ni + C_6H_6 \xrightarrow{Ph_3P} C_{12}H_8NiPPh_3 + C_8H_{12}$	Benzene, 3 days	—	53
$\pi-C_7H_8M(CO)_4 + Ph_2P-$  $\rightarrow (CO)_4M$  $+ C_7H_8$	Benzene, 80°	50	54
$\pi-C_7H_8Mo(CO)_3 + L \rightarrow C_7H_8 + (L)_3Mo(CO)_3$ $L = PF_2Ph$	Ether, 35°	—	55
$PF(Me)(NHMe_2)$	—	54	55, 56
$PF(Ph)(NHMe_2)$	Ether, 35°	51	55, 56
$PF(Me_2NH)_2$	—	24	55, 56
$\pi-C_7H_8Fe(CO)_3 + L \rightarrow L_2Fe(CO)_3 + C_7H_8$ $L = PPh_3$	Ethylcyclohexane 7 hr refluxing	— 29	57, 58
$P(OMe)_3$	110°, 3 hr, N ₂	Quant.	

$\pi\text{-C}_8\text{H}_8\text{Fe}(\text{CO})_3 + \text{PPh}_3 \rightarrow (\text{PPh}_3)_3\text{Fe}(\text{CO})_3 + \text{C}_8\text{H}_8$	Cyclohexane, refluxing, 9 hr	48	57, 58
$\pi\text{-C}_7\text{H}_8\text{M}(\text{CO})_3 + \text{L} \rightarrow \text{L}_3\text{M}(\text{CO})_3 + \text{C}_7\text{H}_8$			
M = Cr, L = diethylenetriamine	Heating without solvent	73	59
Mo, L = diethylenetriamine	Heating without solvent	87	
W, L = diethylenetriamine	Heating without solvent	87	
Mo, PCl_3	Benzene, 80°	80	
Mo, PPh_3	Benzene, 80°	80	
Mo, $\text{PCl}(\text{Ph})_2$	Ether, 25°	80	
Mo, $\text{P}(\text{Cl})_2\text{Ph}$	Ether, 25°	—	
$(\pi\text{-C}_8\text{H}_8)\text{Ru}(\text{CO})_3 + \text{L} \rightarrow \text{L}_2\text{Ru}(\text{CO})_3 + \text{C}_8\text{H}_8$	—	—	60
L = PPh_3 , $\text{P}(\text{OCH})_3\text{CC}_2\text{H}_5$			
$(\pi\text{-C}_8\text{H}_{12})\text{M}(\pi\text{-C}_5\text{H}_5) + \text{S} \begin{array}{c} \text{CF}_3 \\ \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{CF}_3 \end{array} \rightarrow \text{C}_5\text{H}_5\text{M} \begin{array}{c} \text{S} \quad \text{CF}_3 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{S} \quad \text{CF}_3 \end{array}$	Methylcyclohexane, 110°, 1 hr	64	61
M = Co	Methylcyclohexane, 110°, 1 hr	25	
Ir			
$(\pi\text{-C}_8\text{H}_{12})\text{Co}(\pi\text{-C}_5\text{H}_5) + \text{PhC}\equiv\text{CPh} \rightarrow \text{C}_8\text{H}_{12} + \text{Ph}_4\text{C}_4\text{CoC}_5\text{H}_5$	Xylene, 130°	47	62
$\text{Co}(\text{CO})(\pi\text{-C}_8\text{H}_{12})(\text{C}_8\text{H}_{13}) + \text{PR}_3 \rightarrow \text{Co}(\text{CO})(\text{C}_8\text{H}_{13})\text{PR}_3^b$ R = Ph, Me, OPh	Toluene, 20°	60	63
$\text{Co}(\text{CO})(\text{C}_8\text{H}_{13})(\text{PR}_3)^b + \text{PPh}_3 \rightarrow \text{Co}(\text{CO})\text{H}(\text{PPh}_3)_3$	Pentane, 60°	50–60	63
$(\pi\text{-C}_7\text{H}_8)\text{Mo}(\text{CO})_3 + \text{HP}(\text{C}_6\text{F}_5)_2 \rightarrow [\text{HP}(\text{C}_6\text{F}_5)_2]_3\text{Mo}(\text{CO})_3$	Benzene, 80°, 30 min	28	64
$(\pi\text{-C}_8\text{H}_{12})_2\text{Ni} + \text{C}_3\text{H}_5\text{OCOR} \rightarrow (\pi\text{-C}_3\text{H}_5\text{NiOCOR})_2 + \text{C}_8\text{H}_{12}$	Benzene, N ₂ , 25°	80–95	65, 66
R = CX ₃ (X = H, Cl, Br, F)			

* Temperatures, °C.



at $X = H$. In later studies another complex was chosen for the olefin exchange investigation, namely, *trans*-dichloroethylene(pyridine-*N*-oxide)-platinum. Substituent effects in both the pyridine and styrene groups on equilibrium constants of the exchange reactions have been studied (71).

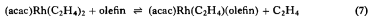


$R = (CH_2)_9CH_3$, C_6H_4X ($X = OMe, Me, H, Cl, NO_2$); $Z = OMe, Me, H, Cl, NO_2, COOMe$

The effect of substituents X , at constant Z , has been compared with the effect of the same substituents in the Z position at constant X .

Increasing electronegativity of X causes the equilibrium to shift to the left; this, however, becomes smaller as the electron attraction effect of Z increases. The equilibrium constant is more affected by Z than X . These results correlate with changes in the $C=C$ stretching modes on the complexes (72). The results obtained have been treated in terms of the MO approximation. It has been assumed that in the dodecene complex the orbital energies change negligibly with respect to those of ethylene, for which the overlap integrals between the $5d6s6p^2$ -hybrid platinum orbitals and the respective bonding and antibonding ligand levels are known. Jaffé's calculation shows that an overlap with π - and π^* -orbitals in the styrene complex (73) is 30% below that in dodecene complex. In other words the latter should be more stable. Electron-releasing substituents increase the stability of the styrene complex as a result of an increasing tendency toward donor-acceptor σ -bond formation; for electron-attractive substituents, such as nitro or carbomethoxy groups, stabilization due to back-donation becomes decisive.

Cramer has arrived at similar conclusions investigating the equilibrium (74):



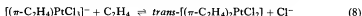
These results, as well as a negligible change of $C=C$ stretching frequencies upon coordination (50–150 cm^{-1} with respect to 200–250 cm^{-1} for acetylene complexes), reflect approximately equal π - and σ -component

contributions to the metal-olefin bonding. Based on a comparatively low dipole moment for the platinum-ethylene bond, Chatt and Duncanson's estimate of the π -contribution is about 30% (33). According to Basolo and Pearson (1), such double bonding could be due to the strong trans effect of the olefin ligands, which could be comparable with that of carbon monoxide or of triphenylphosphine (see also 75).

It is rather interesting to analyze substitution reactions of Zeise type salts. Usually ligands capable of π -bond formation replace ethylene; all other ligands (water, ammonia, halogens, etc.) replace a *trans*-chlorine with respect to ethylene (76). The stability of the complexes with *trans*-amine ligands has been discussed elsewhere (77). The above reactions follow an A-type mechanism, and their rates increase with an increasing nucleophilicity of the attacking reagent. The relative stabilities of platinum-olefin complexes show that the rate of attaining equilibrium is determined by the concentration of both the complex and the substituting olefin, i.e., the reaction is probably bimolecular. The square-planar structure of the complex should favor an increase in coordination number in the transition state. Actually, for the 18-electron octahedral compounds $[(\pi\text{-C}_2\text{H}_4)_2\text{Rh}(\pi\text{-C}_5\text{H}_5)]$ (78) and $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\pi\text{-C}_2\text{H}_4)]\text{PF}_6$ (79), which in general follow a monomolecular substitution path, it has been shown that they do not exchange with labeled ethylene at room temperature over 6 days, whereas $\text{K}[\text{Pt}(\pi\text{-C}_2\text{H}_4)\text{Cl}_3]$, $[(\pi\text{-C}_2\text{H}_4)\text{PtCl}_2]_2$ *trans*- $[(\pi\text{-C}_2\text{H}_4)\text{PtCl}_2\text{tol}]$, and *trans*- $[(\pi\text{-C}_2\text{H}_4)\text{PtCl}_2\text{py}]$ complexes exchange after 1 minute at 0°C (79).

Other authors report that the ethylene-platinum chloride exchange with deuterioethylene is complete in 15 minutes (80). Sometimes the reactions are so fast that it is rather difficult to employ the commonly used methods for kinetic investigations. For example, the rate of the fast ethylene exchange for Zeise's salt (81) is more than 70 sec^{-1} . NMR spectroscopy has been employed by Cramer for investigating exchange in rhodium compounds (78), and by Vrieze, Volger, and Praat (82) for the diene-rhodium and -iridium complexes $[(\text{diene})\text{M}(\text{Cl})\text{L}]$, where the diene is cycloocta-1,5-diene or norbornadiene, $\text{L} = \text{PPh}_3$ or AsPh_3 . An NMR study of the ethylene exchange (83) allows a distinction between coordinated and noncoordinated olefin. If substitution takes place, then the coordinated and free ligand peaks broaden, producing a large absorption band between the signals due to the ligand and the free olefin protons. It has been shown that the extent of such broadening depends on the concentration of the attacking agent, i.e., a substituting olefin is participating in the limiting reaction step.

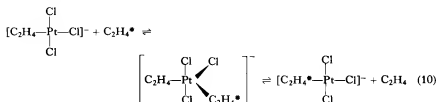
In Cramer's opinion (81), exchange may occur as a sequence of trans migrations via a *trans*-bis(ethylene)platinum chloride intermediate:



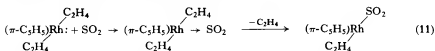
However, the study failed to reveal bis(ethylene)platinum chloride in the mixture. A similar *trans*-chlorine substitution should be easier with the strong trans effect of an olefin ligand. Chatt and Wilkins have prepared this compound (84) and found that it rapidly releases ethylene at room temperature:



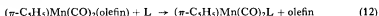
Another mechanism for explaining the rate dependence on concentration of the olefin involves ordinary A-type substitution:



It has been suggested (81) that an analogous mechanism is valid also for olefin substitution in square-planar complexes of platinum, rhodium, and iridium. As mentioned above, $[(\pi\text{-C}_2\text{H}_4)_2\text{Rh}(\pi\text{-C}_5\text{H}_5)]$ does not exchange olefin with labeled ethylene. However, this complex readily reacts with SO_2 (85). This is one of the few examples of an electrophilic ligand replacement. π -Cyclopentadienylbis(ethylene)rhodium is formally a five-coordinate complex with an electron pair occupying a sixth coordination site. In this light the following A-type mechanism has been proposed:



Far less information is available on olefin substitution in closed-shell octahedral complexes. Angelici and Loewen (86) have studied the kinetics of the reaction



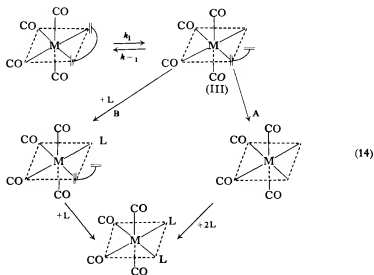
The reaction rate is independent of concentration of L, and the positive activation entropy favors a D-type mechanism. The following reactivity

order has been established: ethylene < norbornadiene < norbornylene < cyclooctene < propylene < cyclopentene < 1-pentene \approx cycloheptene. Ethylene has been found to exchange much faster than CO does in $(\pi\text{-C}_8\text{H}_8)\text{Mn}(\text{CO})_3$.

Polydentate olefin substitution has been studied mainly in Group VIB metal complexes. The compound $\text{Mo}(\text{CO})_4(\pi\text{-C}_8\text{H}_{12})$ undergoes substitution (87, 88) with 1,2-bis(diphenylphosphino)ethane, 2,2'-dipyridyl, 1,10-phenanthroline, and triphenylphosphine, -arsine, and -stibine, producing $\text{Mo}(\text{CO})_4\text{L}_2$ or $\text{Mo}(\text{CO})_4\text{D}$, where L and D are, respectively, the mono- and bidentate ligands. The reaction rate is described by the equation

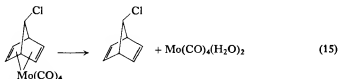
$$v = k_1[\text{Mo}(\text{CO})_4(\pi\text{-C}_8\text{H}_{12})] + k_2[\text{Mo}(\text{CO})_4(\pi\text{-C}_8\text{H}_{12})][\text{L}] \quad (13)$$

which is specific for ligand substitution in square-planar "inorganic" complexes. However, the present authors assume that k_1 describes dissociation of one of the metal-diene ligand bonds rather than a reaction with solvent, analogously to the planar complexes. In fact the activation entropy of this reaction step is positive, which provides more degrees of freedom in a transition state, and is characteristic of monomolecular D-type reactions. The activation energy of this step (25 kcal/mole) is very close to that of dissociative substitution in $\text{Cr}(\text{CO})_4(\text{dipy})$ (89). The second-order rate constant describes a bimolecular reaction step. The authors propose the mechanism shown in the scheme.



This involves a fast preequilibrium step with complex (III) as an intermediate having a lower coordination number. The latter then reacts either by a simple dissociative mechanism (path A) or through a partial dissociation (path B).

Recently an indication of path A has been shown by investigating solvolysis of the 7-substituted norbornadiene complexes of Cr, Mo, and W (90). It was found that in an 80% acetone-water solution at 25°C, $(\pi\text{-C}_7\text{H}_7\text{Cl})\text{Mo}(\text{CO})_4$ gives free 7-norbornadienol instead of the expected $(\pi\text{-C}_7\text{H}_7\text{OH})\text{Mo}(\text{CO})_4$. Moreover, the solvolysis rate constant was of the same order of magnitude as that for free 7-chloronorbornadiene. All these data support fast dissociation of the type

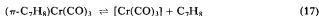


followed by subsequent slow solvolysis of the resulting 7-chloronorbornadiene. The degree of dissociation is determined by the solvent, attaining 50% in 90% acetone-water. It was also found that dissociation in the series of norbornadiene complexes varies in the order: $\text{Mo} > \text{Cr}, \text{W} < \text{Fe}$.

Substitution of the tridentate cycloheptatriene ligand has been studied by two groups of authors. Strohmeier and Mittnacht have found (91) that exchange of $(\pi\text{-C}_7\text{H}_8)\text{Cr}(\text{CO})_3$ with ^{14}C -cycloheptatriene follows the equation

$$v = k_1[(\pi\text{-C}_7\text{H}_8)\text{Cr}(\text{CO})_3] + k_2[(\pi\text{-C}_7\text{H}_8)\text{Cr}(\text{CO})_3][\text{C}_7\text{H}_8^*] \quad (16)$$

where $k_1 \gg k_2$. Dissociation is a limiting reaction step



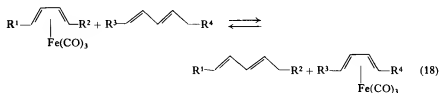
which is followed by fast formation of the final product. Activation parameters have been calculated for each step. Based on a positive ΔS for the second stage, the authors assume that at least two of the three metal-ligand "old" bonds cleave in the transition state. Owing to free rotation there are more degrees of freedom in the transition state and hence the higher activation entropy.

Pidcock and Taylor (92) have studied the kinetics of cycloheptatriene substitution in $(\pi\text{-C}_7\text{H}_8)\text{M}(\text{CO})_3$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) by trimethylphosphite. The second-order rate constants change noticeably with the

nature of the central metal atom [$\text{Cr} \ll \text{Mo} > \text{W}$ (1:2210:355)]. A bimolecular mechanism with a seven-coordinated transition state has been assumed. In their opinion another mechanism may occur via successive reduction of the coordinative ability of the C_7H_8 ligand. Such a pathway is quite probable since there are stable cycloheptatriene complexes in which it acts as a bi- or a monodentate ligand (93, 94).

Thus the mechanism for substitution involving cycloheptatriene changes markedly with the nature of the substituting ligand. Apparently exchange with labeled ligands cannot occur through a seven-coordinated transition state because the entering C_7H_8 ligand is rather bulky.

Substitution of polydentate olefins has been also studied with π -complexes of iron (95). Substituted derivatives of butadieneiron tricarbonyl have been found to undergo the following transformation (96).



At complex–diene ratios of 1:1, 2:3, and 1:2 the reaction is second order, and first order in each component. An associative mechanism has been suggested. It was shown that with a monoolefin iron complex the substitution reaction follows first-order kinetics with a rate independent of diene concentration.

Substitution of cyclooctatetraene in $(\text{COT})\text{Fe(CO)}_3$ by phosphorus-containing ligands in decalin has been studied under pseudo-first-order reaction conditions. The observed rate constant is given by the relation

$$k_{\text{obs.}} = k_2[\text{substituting ligand}] \quad (19)$$

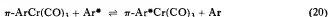
where k_2 is the second-order rate constant. Activation parameters of the reaction are characteristic of A-type reactions. It has been found that substitution of COT occurs much faster than for cycloheptatriene.

C. π -Arene-Transition Metal Complexes

In arene-transition metal complexes the ligand is considered to occupy three coordination sites. With this view it is interesting to compare the results of arene substitution with the above data for cycloheptatriene. The

high delocalization energy of an arene makes it hard to expect a successive diminishing of coordinative ability with liberation of one or two double bonds. However, it should be pointed out that stable complexes are known with a single double bond of an arene ligand participating in bonding with a metal (97).

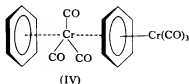
In one of the earlier studies, Strohmeier and Mittnacht found (98) that the exchange of benzenechromium tricarbonyl with labeled benzene is essentially slower than the corresponding reaction with $(\pi\text{-C}_7\text{H}_8)\text{Cr}(\text{CO})_3$. Kinetics of the isotopic exchange reaction



show that its mechanism is different (99) from the similar reaction of the cycloheptatriene complex. The rate of reaction is described by a kinetic equation characteristic of the two independent reactions

$$v = k_1[\pi\text{-ArCr}(\text{CO})_3]^2 + k_2[\pi\text{-ArCr}(\text{CO})_3][\text{Ar}^*] \quad (21)$$

where $k_1 \gg k_2$. There is a very slight dependence of the observed rate constant on $[\text{Ar}^*]$. Generally the reaction is determined by the second-order rate constant. In the limiting step the reaction involves formation of an intermediate $(\pi\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ with fast cleavage to benzene and an active $\text{Cr}(\text{CO})_3$ fragment. The latter reacts with labeled C_6H_6 to give the final reaction product. The following structure of the intermediate has been proposed:



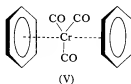
It has been assumed that in the transition state, the bond between the two $(\pi\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ molecules is a result of an overlap between the occupied d -atomic orbitals of chromium and π^* -orbitals of the arene ligand. In the authors' opinion such transition states in which the arene acts as a charge acceptor are in good agreement with the data on dipole moments of arene-metal tricarbonyls. Increase in solvent polarity causes an approximately twofold increase in the reaction rate (100) in passing from heptane to tetrahydrofuran.

The effects of both the central metal atom and the arene substituents on the reaction rate have also been studied (101). The exchange rate increases

in the series $\text{Cr} \ll \text{W} \leq \text{Mo}$, which can be explained by the relatively high abilities of molybdenum and tungsten to increase their coordination number in the transition state.

Electron-releasing substituents in the ring increase the reaction rate. There is a linear dependence between the rate constant and the σ -constants of the substituents.

The second term in Eq. (21) describes an alternative reaction mechanism—a bimolecular A-type substitution via the transition state (V) as the limiting step.



This mechanism is similar to that proposed for cycloheptatriene replacement in $(\pi\text{-C}_7\text{H}_8)\text{Cr}(\text{CO})_3$ by trimethyl phosphite. By analogy with the isotopic exchange of cycloheptatriene, the probability of a seven-coordinated transition state is rather low, which provides an explanation for the low rate constant k_2 . In other words, using Pearson's terminology (102), the arene can be regarded as a soft nucleophile towards bimolecular reactions, while reactivity of the complexes of the Group VIB metals is defined generally by the nucleophile polarizability. The phosphorus-containing ligands are the most suitable nucleophiles for such metals. Moreover, Basolo *et al.* (103) have found that arene-molybdenum tricarbonyl exchanges much faster with different tertiary phosphines than with arene. On the other hand, increasing phosphine basicity enhances the substitution rate. The authors have suggested a bimolecular A-type mechanism:

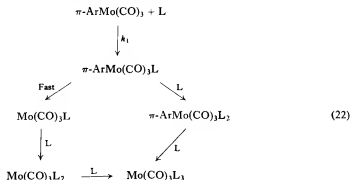

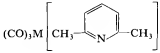



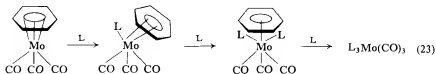
TABLE II
SUBSTITUTION OF ARENE LIGANDS

Reaction	Reaction conditions*	% Yield	References
$\text{Cr}(\pi\text{-C}_6\text{H}_6)_2 + \text{tert}-(\text{C}_4\text{H}_9\text{O})_2 \rightarrow (\text{tert}-\text{C}_4\text{H}_9\text{O})_4\text{Cr}$	Benzene 90°, 20 hr	80	105
$(\pi\text{-C}_6\text{H}_6)\text{Cr}(\pi\text{-C}_5\text{H}_5) + \text{C}_7\text{H}_8 \rightarrow (\text{C}_6\text{H}_6\text{CrC}_7\text{H}_8)^+ + \text{C}_5\text{H}_6$	N ₂ , AlCl ₃	75	106
$\text{Cr}(\pi\text{-C}_6\text{H}_6)_2 + \text{C}_7\text{H}_8 \rightarrow (\text{C}_6\text{H}_6\text{CrC}_7\text{H}_8)^+$	N ₂ , AlCl ₃	—	106
$\text{Cr}(\pi\text{-C}_6\text{H}_6)_2 + \text{CO} \rightarrow \text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$	—	—	107
$\text{Cr}(\pi\text{-C}_6\text{H}_6)_2 + \text{Cr}(\text{CO})_6 \rightarrow (\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$	Benzene, 220°, 12 hr	25	108, 109
$\text{Cr}(\pi\text{-C}_6\text{H}_6)_2 + \text{PF}_3 \rightarrow \text{Cr}[(\text{PF}_3)_3]_6$	210°–230°, 350 atm, 15 hr	10	110
$(\pi\text{-C}_6\text{H}_6)\text{M}(\text{CO})_3 + \text{L} \rightarrow \text{L}_3\text{M}(\text{CO})_3$			
M = Cr L = (C ₆ H ₅ O) ₃ P	240°, 1.5 hr	69	111
Cr (C ₆ H ₅ O) ₃ P	240°, 1.5 hr	100	
Mo (C ₆ H ₅ O) ₃ P	240°, 1.5 hr	59	
$[\pi\text{-1,3,5-(CH}_3)_3\text{C}_6\text{H}_3]\text{M}(\text{CO})_3 + \text{CH}_3\text{-}$  $\text{-CH}_3 \rightarrow$ 			
M = Cr	60°, 2 hr	100	112
Mo	60°, 2 hr	100	
W	60°, 3 hr	100	
$[\pi\text{-1,3,5-(CH}_3)_3\text{C}_6\text{H}_3]\text{Mo}(\text{CO})_3 + \text{tripy} \rightarrow \text{tripy Mo}(\text{CO})_3$	20°, 2 hr	100	112
$(\pi\text{-C}_6\text{H}_6)\text{Cr}(\pi\text{-C}_5\text{H}_5) + \text{L} \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Cr}(\pi\text{-C}_{10}\text{H}_6\text{R}_2)$	Benzene N ₂ , 25°	43	113, 114
L =  , C ₁₀ H ₆ R ₂ ; R = Me, Ph			

$(\pi\text{-CH}_3\text{C}_6\text{H}_5)\text{Cr}(\text{CO})_3 + \text{C}_6\text{H}_5\text{NMe}_2 \rightarrow (\text{CO})_3\text{Cr}[(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_5]_3$ $+ (\text{CH}_3)_2\text{AsC}_6\text{H}_5 \rightarrow [(\text{CH}_3)_2\text{AsC}_6\text{H}_5]_3\text{Cr}(\text{CO})_3$ $+ \text{P}(\text{C}_6\text{H}_5)_3 \rightarrow [\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cr}(\text{CO})_3$	Refluxing, 12 hr 150°, 1 hr 160°, 2 hr	— 41 10	115
$(\pi\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3 \xrightarrow[\text{hv}]{\text{CH}_3\text{OH}} \text{Cr}(\text{OCH}_3)_3 + \text{C}_6\text{H}_6 + \text{CO}$	CH ₃ OH	—	116
$\text{Cr}(\pi\text{-C}_6\text{H}_6)_2 + \text{Cr}(\text{CO})_6 \rightarrow (\pi\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$	Benzene, 220°	—	117
$(\pi\text{-C}_6\text{H}_6)_2\text{M} + \text{tripry} \rightarrow \text{M}(\text{tripry})_3 + \text{CO}$ $\text{M} = \text{Cr, Mo}$	Cyclohexane, 160°	—	118
$(\pi\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3 + \text{L} \rightarrow \text{Cr}(\text{L})_3 + \text{CO} + \text{C}_6\text{H}_6$ $\text{L} = \text{dipy; phen}$	Cyclohexane, 180°	—	118
$(\pi\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3 + \text{NH}_3 \rightarrow [(\text{NH}_3)_3\text{Cr}(\text{CO})_3] + \text{C}_6\text{H}_6$	Cyclohexane, 60°	—	118
$[(\pi\text{-C}_6\text{H}_5\text{C}_6\text{H}_5)\text{Cr}(\pi\text{-C}_6\text{H}_6)]\text{AlCl}_4 + \text{FC}_6\text{H}_4\text{C}_6\text{H}_5 \rightarrow [\text{C}_6\text{H}_5\text{C}_6\text{H}_5\text{CrC}_6\text{H}_5\text{C}_6\text{H}_4\text{F}]^+$	—	—	119, 120
$(\pi\text{-C}_6\text{H}_5\text{C}_6\text{H}_5)_2\text{CrCl} + \text{dipy} \rightarrow [(\text{dipy})_3\text{Cr}]\text{Cl} + \text{C}_6\text{H}_5-\text{C}_6\text{H}_5$	CH ₃ OH	—	121
$\text{Cr}(\pi\text{-C}_6\text{H}_5)_2 + 1,3,5\text{-(CH}_3)_3\text{C}_6\text{H}_3 \rightarrow [1,3,5\text{-(CH}_3)_3\text{C}_6\text{H}_3]_2\text{Cr}$	—	—	122
$(\pi\text{-C}_6\text{H}_6)\text{Cr}(\pi\text{-C}_6\text{H}_5\text{C}_6\text{H}_5) + \text{Ar} \xrightarrow{\text{KI}} \text{Ar}_2\text{CrI}$ $\text{Ar} = \text{C}_6\text{H}_6$ $1,3,5\text{-(CH}_3)_3\text{C}_6\text{H}_3$ $\text{CH}_3\text{C}_6\text{H}_5$ Tetraline	Benzene, AlCl ₃ , 80°, 2 hr 130°, AlCl ₃ , 1.5 hr 120°, AlCl ₃ , 25 min 120°, AlCl ₃	— 70 85 86	123
$(\pi\text{-C}_6\text{H}_6)_2\text{Cr} + \text{C}_6\text{H}_5-\text{C}_6\text{H}_5 \rightarrow (\pi\text{-C}_6\text{H}_5\text{C}_6\text{H}_5)_2\text{Cr}$	AlCl ₃ , 115°, 0.5	41	123
$(\pi\text{-C}_6\text{H}_5-\text{C}_6\text{H}_5)_2\text{Cr} + \text{C}_6\text{H}_6 \rightarrow (\pi\text{-C}_6\text{H}_6)_2\text{Cr}$	80°, AlCl ₃ , 3 hr	0	123
$[(\pi\text{-C}_6\text{H}_6)\text{Cr}(\pi\text{-C}_6\text{H}_5-\text{C}_6\text{H}_5)]\text{AlCl}_4 + \text{C}_6\text{H}_5-\text{C}_6\text{H}_5 \rightarrow$ $[(\pi\text{-C}_6\text{H}_5-\text{C}_6\text{H}_5)_2\text{Cr}]\text{AlCl}_4$	AlCl ₃ , 120°, 1 hr	52	124
$\pi\text{-ArCr}(\text{CO})_3 + \text{Ar}' \rightarrow \text{Ar}'[\text{Cr}(\text{CO})_3]_2$ $\text{Ar} = \text{diphenyl, benzpyrene, stilbene}$	160°, N ₂	70	125
$\text{ArCr}(\text{CO})_3 + \text{Ar}' \rightarrow \text{Ar}'\text{Cr}(\text{CO})_3 + \text{Ar}$ $\text{Ar}' = \text{C}_6\text{H}_5\text{OH, C}_6\text{H}_5\text{COOH, C}_6\text{H}_5\text{COOR, C}_6\text{H}_5\text{NH}_2, \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$	140°–180°, N ₂	—	126

* Temperatures, °C.

The following scheme has been proposed for arene substitution by tertiary phosphines:



Pidcock, Smidt, and Taylor have proposed the same mechanism for substitution of arene with trimethyl phosphite (104).

Thus substitution of the arene ligand is a multistep process. Its first step, a bimolecular reaction, is the rate-determining stage; then a number of fast reactions follow with as yet uncertain mechanism.

The examples considered do not cover all the known data on arene-ligand substitution. Many studies (see Table II) deal with ligand substitution as a synthetic method for transition metal compounds. An important conclusion can be drawn based on these investigations. In the bis-arene complexes usually both ligands undergo substitution, and aluminum halides stimulate the reaction. Substitution in arene-chromium tricarbonyl usually involves the arene ligand, independent of the nature of the attacking reagent. But in photochemical reactions, CO group substitution takes place. In "mixed" cyclopentadienyl(arene)-metal complexes substitution involves the arene moiety.

In this section (Section III) we have discussed substitution reactions of ligands in the first class of complexes (see Section II). Except for acetylene complexes, this class exhibits a tendency to react by an associative mechanism with increase of coordination number in the transition state. Data on monodentate olefins are in agreement with this suggestion. Substitution of polydentate ligands is more complicated and usually depends upon the nature of both the replacing ligand and of a fragment to be substituted. Thus substitution involves competition between both possible mechanisms.

Quantitative data favors the associative mechanism as being more predominant, its role becoming more likely with increasing electron donor ability of the substituting ligand. Acetylenes undergo a D-type substitution, although at least for platinum complexes a bimolecular associative substitution might be expected, based on the transition-state geometry. Probably, the ability of Pt(0) to form complexes with a low coordination number is a reason for this behavior. Strong trans-directing ligands (CO, PPh₃) should

also favor a dissociative mechanism. It should be noted, however, that the experimental results available on π -acetylene substitution are rather insufficient to provide a basis for a final conclusion.

IV

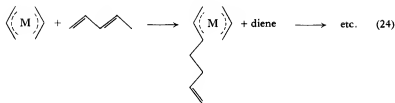
π -COMPLEXES WITH LIGANDS UNSTABLE IN A NONCOORDINATED STATE

A. π -Allyl Substitution and Transfer Reactions

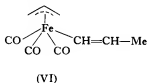
Within the last decade π -allyl coordination chemistry has developed very extensively. π -Allyl complexes have been characterized for nearly all of the transition elements.

The synthesis and properties of π -allyl transition metal complexes have been discussed elsewhere (127-129). We shall draw attention to the most interesting properties of π -allyl complexes such as structure, coordinative unsaturation of the metal, and the ability of the π -allyl ligand to enter into intermolecular rearrangements.

According to X-ray analysis (130-134) the π -allyl group can be regarded as occupying two coordination sites. The palladium, nickel, and platinum allyl halide complexes, and their bis(π -allyl) derivatives, have square-planar structures. π -Allyliron tricarbonyl halides, and probably cobalt complexes also, have structures based on a distorted octahedron with coordination numbers equal to 6 and 5, respectively. The "pure" π -allyl complexes $M(C_3H_5)_n$ are usually rather unstable (except when $M = Pd$ and Pt all such complexes readily decompose at room temperature under an inert atmosphere). For the majority of π -allyl compounds, $M(\pi-C_3H_5)_n$, the metal atoms do not obey the effective atomic number rule. Unlike other analogous π -complexes [for example, $M(\pi-C_5H_5)_n$ and $M(\pi-C_6H_6)_n$] allyl complexes easily undergo substitution reactions with various ligands (135). Hence these complexes find use as catalysts for olefin polymerization (136). It is assumed (137) that the first step involves replacement of the π -allyl group by a diene to give a new substituted π -allyl complex.

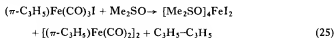


At low temperatures, carbon monoxide replaces all three allyl groups in triallylchromium to give $\text{Cr}(\text{CO})_6$ (138). The reaction also affords the compound $(\pi\text{-C}_3\text{H}_5)_2\text{CrCO}$, which the authors failed to isolate but confirmed by mass spectra. In the same manner, CO replaces one allyl group in tris(π -allyl)iron to give (VI) (139).



Formation of the σ -propenyliron derivative is rather unusual, and has no analogy in the chemistry of π -allyl complexes. Probably in such complexes the facility to partially or completely replace the π -allyl ligand by CO and other groups can be explained by electron deficiency at the metal atom.

Another condition which is essential in enhancing the reactivity of π -allyl compounds towards substitution is the easiness of the π, σ -rearrangement for the allyl ligand (135, 140-146). When the π -allyl ligand is converted entirely to its σ -bonded state there occurs a consequential increase of the metal's coordinative unsaturation. Hence dimethyl sulfoxide readily substitutes all the ligands in the electronically and coordinatively saturated complex $(\pi\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_3\text{I}$ (147).

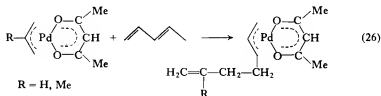


π, σ -Perturbations of the π -allyl group occur in the presence of electron-releasing ligands such as phosphines, arsines, and stibines (141, 142). But the process may also take place without these agents being present, simply at elevated temperatures (143). Depending upon the concentration of donor or temperature, allyl complexes in solution may convert to the π, σ - or σ -bonded allyl derivatives. Ease of transformation is determined both by

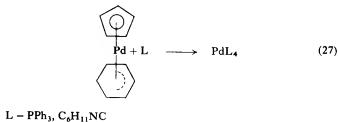
the relative strength and concentration of the donor and by the nature of the metal. Wilke has shown (145) that the dimeric π -allylnickel halides undergo π, σ -perturbations in the presence of Et_3P at a reaction ratio of $\text{P}:\text{Ni} = 2:1$. Triphenylphosphine does not cause this transformation. With dimeric π -allylpalladium halides, however, the π -allyl ligand converts to the σ -bonded state even in the presence of PPh_3 ($\text{P}:\text{Pd} = 2:1$). In the case of Et_3P , the process occurs at a ratio $\text{P}:\text{Pd} = 1:1$. At large donor concentrations fast exchange of the donor molecules (146) accompanies the π, σ -allyl perturbation. With weak donors (AsPh_3 , SbPh_3) the reaction proceeds as an I_a exchange via a five-coordinate transition state. Probably an analogous mechanism operates in the metathetical replacement of μ -halide bridges in dimeric allylpalladium halides (148).

Substitution of CO in $(\pi\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_3\text{I}$ also involves an associative process (149), while Heck (150) has found that CO replacement by triphenylphosphine in five-coordinate $(\pi\text{-C}_3\text{H}_5)\text{Co}(\text{CO})_3$ is a D-type reaction in spite of the coordinative unsaturation of the metal in the starting complex.

Substitution of π -allyl groups by other hydrocarbon ligands has been studied in less detail. Formally such reactions may resemble the recently reported interaction of π -allylpalladium acetylacetonate with butadiene (151) in which the diene inserts into the $\text{Pd}-\text{C}_3\text{H}_5$ bond.

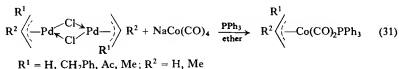


π -Allyl and π -cyclopentadienyl ligands have been replaced by triphenylphosphine or cyclohexylisocyanide in π -cyclohexenyl- π -cyclopentadienyl-palladium (152)

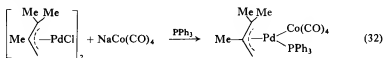


It has been shown that $\text{Fe}(\text{CO})_5$ accumulates in solution (GLC and polarography), and it reacts considerably more slowly with π -allylpalladium chloride than does iron enneacarbonyl (158).

Another example of π -allyl ligand transfer has been described recently by Heck (159). Treatment of π -allyl derivatives of palladium chloride with $\text{NaCo}(\text{CO})_4$ in ether gives π -allyl cobalt complexes.

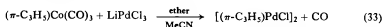


The reaction products were isolated as stable phosphine derivatives. In the reaction with 1,1,2-trimethyl- π -allylpalladium chloride Heck isolated a compound whose structure probably resembles that of the intermediate in other allyl transfer reactions (159):



However, the structure of the complex obtained is assumed on the basis only of the IR spectrum and on elementary analysis. Low solubility of the complex prevented an NMR study.

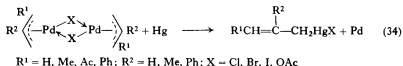
Heck (159) has also carried out the reverse reaction— π -allyl ligand transfer from cobalt to palladium. π -Allylcobalt tricarbonyl reacts readily with lithium trichloropalladite in ether-acetonitrile.



Using this reaction Heck has prepared some substituted binuclear π -allylpalladium chlorides which are not produced by the common synthetic procedures.

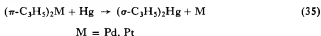
The term π, π -transfer has been proposed for π -allyl ligand transfer from one transition metal to another. Such processes differ from those giving σ -allyl derivatives (160), which are termed π, σ -transfer processes. The latter have been studied in detail (161) for π -allylnickel, -palladium, and -platinum complexes interacting with metallic mercury. It has been shown that binuclear π -allylpalladium complexes rapidly react with mercury in

benzene at room temperature to give quantitatively the respective allyl-mercury derivatives and metallic palladium.



The authors suggest this method as a preparative procedure for allyl-mercury compounds starting from olefins and dienes via the π -allylpalladium complexes.

The same study describes the reaction of bis(π -allyl)palladium and -platinum complexes with metallic mercury (161).



It has been found that under similar, and even more drastic conditions, the nickel complexes do not react with metallic mercury. Formally the reaction of allylpalladium complexes with metallic mercury might be regarded as a redox process. However, since metals which behave as stronger reducing agents than mercury do not enter the π -allyl transfer reaction⁹ this argues against a simple redox mechanism for π -allyl transfer from palladium to mercury.

The reaction is specific in that the allyl group retains its configuration in the course of transfer. Thus reactions of metallic mercury with an asymmetrically substituted π -allylpalladium chloride (for example, crotylpalladium chloride) might equally afford both *cis*- and *trans*-2-butenylmercury chloride isomers, as well as the 1-butenyl compound. Hence generally three compounds could be expected in the reaction. However, it has been found (161) that essentially the reaction yields only *trans*-crotylmercury chloride (based on infrared spectra). In the case of 1-phenyl- π -allylpalladium chloride and 1-acetyl-2-methyl- π -allylpalladium chloride, again only the respective γ -substituted *trans*-allylmercury halides have been found. Since such conditions do not allow the allyl rearrangement (162), formation of the *trans*-allylmercury derivatives is evidence that the

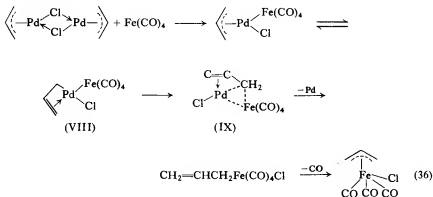
⁹ Attempts were made to extend the π, σ -transfer of allyl ligand from palladium to other metals (161) (magnesium, copper, zinc, cadmium, and liquid gallium). It has been found that these metals do not form their respective allyl derivatives in reaction with π -allylpalladium chloride.

syn form of the π -allyl ligand remains fixed during transfer. We can assume (161) formation of an intermediate (VII) as a result of asymmetric cleavage of the μ -halide bridges in the dimer of π -allylpalladium chloride on treatment with mercury.



The π,π -allyl ligand transfer from palladium to iron is convenient for investigating the reaction mechanism. It has been established (158) that on mixing the reagents, a green intermediate rapidly forms and slowly converts to the reaction products. This permits employment of some physicochemical methods in the study of reaction.

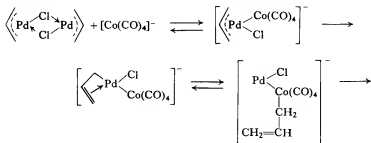
The moiety $\text{Fe}(\text{CO})_4$, generated from $\text{Fe}_2(\text{CO})_9$, behaves as a nucleophile cleaving the μ -halide bridges of $[(\pi\text{-C}_3\text{H}_5)\text{PdCl}]_2$. Structures of the intermediates have been deduced from IR and nuclear γ -resonance (Mössbauer) spectra. An NMR study of the reaction mixture showed that the intermediates (VIII) and (IX), with π,σ - and σ -bonded allyl groups, respectively, gradually form. Subsequent reaction has been discussed in terms of cis insertion of $\text{Fe}(\text{CO})_4$ into the $\text{Pd}-\text{C}$ σ -bond (163), or cis migration of the σ -bonded allyl group from palladium to iron accompanied by CO evolution and precipitation of metallic palladium.



An analogous scheme has been proposed (161) for the subsequent transformations of complex (VII) in the π, σ -transfer of allyl ligand from palladium to mercury.

In both schemes cis insertion is the most hypothetical step. Cossee has assumed (164) that similar processes take place during olefin polymerization in the presence of Ziegler-Natta catalysts, and in some other reactions catalyzed by the transition metal compounds. This author came to the conclusion (165) that the d orbitals of the metal combine with the migrating group to facilitate such processes. In the course of π -allyl transfer the palladium orbitals overlap with the antibonding orbitals of double bond of the σ -bonded allyl group so as to favor an insertion reaction.

It should be noted that Heck (159) does not discuss details of the ligand transfer other than to regard it as involving a 1,2-shift of the allyl group probably via a σ -bonded palladium intermediate.



A comparison of this scheme with those described above shows their similarity. In both cases there are three distinct steps necessary for and specific to the transfer of π -bonded hydrocarbon ligands: coordination of an attacking agent by a substrate molecule, a π, σ -rearrangement of the ligand, and finally ligand transfer itself proceeding as cis insertion.

B. Transfer of the π -Tetraphenylcyclobutadienyl Ligand

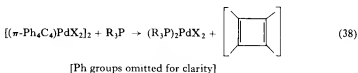
Existence of cyclobutadiene as the simplest cyclic hydrocarbon with conjugated double bonds was predicted by Hückel in the 1930s. Until recently, however, all attempts to prepare this compound ended in failure. In 1956 Longuet-Higgins deduced (166) that coordination of cyclobutadiene with a transition metal should stabilize its unstable triplet state.

The existence of complexes of tetraphenyl-, tetramethyl-, and unsubstituted-cyclobutadiene (167) has confirmed the prediction and greatly advanced both theoretical organic chemistry and the study of transition metal π -complexes.

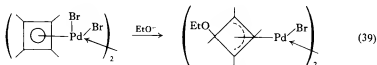
Syntheses and properties of cyclobutadiene-transition metal complexes have been discussed in detail by Maitlis (167). Brown (168), and others (169) have reviewed the metal-ligand bond in terms of the MO approximation. The main bonding in these complexes is due to an overlap of the two degenerate nonbonding cyclobutadiene orbitals with sp^d^2 hybrid metal atomic orbitals.

The X-ray study (170, 171) established a planar structure for the cyclobutadiene ring with C—C distance equal to 1.46 Å and angles of 90°. All the M—C distances are equivalent and close to those observed in ferrocene. The phenyl and methyl substituents are distorted from the ring plane and bent towards the metal atom. If one assumes that cyclobutadiene occupies two coordination sites then in the known tetraphenylcyclobutadiene-nickel and -palladium complexes the metal atom has a coordination number of 5. This suggests coordinative unsaturation for the metal and *a priori* one may expect an associative substitution for such complexes.

It has been found that the direction of nucleophilic attack is determined by the nature of the attacking reagent. Phosphines, for example, attack the palladium atom, replacing the π -ligand and producing a triphenylphosphine-palladium chloride complex (172–174).



According to theory (102), phosphine (soft base) preferably attacks the palladium atom (soft acid). Less polarized but more basic ethoxy anion (hard base) reacts in a somewhat different manner (175).



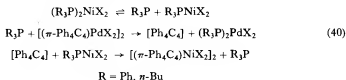
Experimental data available on tetraphenylcyclobutadiene transfer are summarized in Table III.

TABLE III
SUBSTITUTION AND TRANSFER OF THE TETRAPHENYLCYCLOBUTADIENE LIGAND

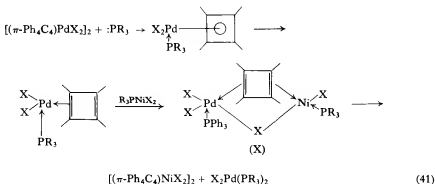
Reactions	Reaction conditions*	% Yield	References
$[\{\pi-(C_6H_5)_4C_4\}PdBr_2]_2 + Ni(CO)_4 \rightarrow [\{\pi-(C_6H_5)_4C_4\}NiBr_2]_2 + Pd + CO$	Benzene, 80°, 2.5 hr	47	176, 182
$[\{\pi-(C_6H_5)_4C_4\}PdBr_2]_2 + Fe(CO)_5 \rightarrow [\pi-(C_6H_5)_4C_4]Fe(CO)_3$	Xylene, 130°, 30 min	88	176, 182
$[\{\pi-(C_6H_5)_4C_4\}PdBr_2]_2 + (C_5H_5)_2Co \rightarrow C_5H_5Co[\pi-(C_6H_5)_4C_4]$	Xylene, 130°, 30 min	12	176, 182
$[\{\pi-(R'C_6H_4)_4C_4\}PdX'_2]_2 + (R'_3P)_2NiX''_2 \rightarrow [(\{R'C_6H_4\}_4C_4NiX''_2)]_2$	Chlorobenzene, 80°, 2 hr		174
$R' = H \quad X' = Cl \quad R'' = Bu \quad X'' = Br$		90	
$p\text{-}Cl \quad Br \quad Bu \quad Br$		82	
$p\text{-}MeO \quad Br \quad Bu \quad Br$		72	
$p\text{-}Me \quad Br \quad Bu \quad Br$		77	
$H \quad Cl \quad Bu \quad Br$		73	
$[\{\pi-(C_6H_5)_4C_4\}PdX_2]_2 + M(CO)_6 \rightarrow [(C_6H_5)_4C_4M(CO)_5X]_n$	Benzene, 80°, 67 hr		177
$M = Mo \quad X = I$		9	
$Mo \quad Br$		7	
$W \quad I$		—	
$[\{\pi-(C_6H_5)_4C_4\}PdC_3H_5]Br + Co_2(CO)_8 \rightarrow [\pi-(C_6H_5)_4C_4]CoC_3H_5$	Benzene, 80°, 1 hr	10	178
$[\{\pi-(C_6H_5)_4C_4\}PdBr_2]_2 + [C_5H_5Fe(CO)_2]_2 \rightarrow [\pi-(C_6H_5)_4C_4]Fe(CO)_3$	Xylene, 130°, 1 hr	11	177
$[\{\pi-(C_6H_5)_4C_4\}PdBr_2]_2 + Co_2(CO)_8 \rightarrow [\pi-(C_6H_5)_4C_4]Co(CO)_2Br$	CH ₂ Cl ₂ , 25°, 45 hr	60	180
$[\{\pi-(C_6H_5)_4C_4\}PdX_2]_2 + [C_5H_5M(CO)_3]_2 \rightarrow C_5H_5MX(CO)[\pi-(C_6H_5)_4C_4]$	—	—	181
$M = Mo, W; X = Cl, Br.$			

* Temperatures, ° C.

As seen from Table III, π -tetraphenylcyclobutadienepalladium chloride serves as the cyclobutadienylating reagent. It is a specific reaction in that it is determined by the nature of the solvent. Ligand transfer proceeds satisfactorily only in hydrocarbons at elevated temperatures. The π -ligand transfer can be accomplished either with metal carbonyls or their cyclopentadienyl derivatives, and with $(R_3P)_2NiX_2$. Two different mechanisms have been proposed for this reaction (174). The first involves cleavage of the palladium–tetraphenylcyclobutadiene bond (a D-type mechanism).



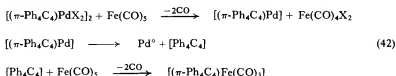
The alternative scheme is as follows (180):



It is known that $(R_3P)_2NiBr_2$ readily releases a triphenylphosphine group in benzene (183). The next step in (41) is analogous to that of substitution of polyene ligands in the presence of strong electron donors. A released double bond coordinates the nickel atom to form an intermediate complex (X) so that an intramolecular transfer of the ligand is possible.

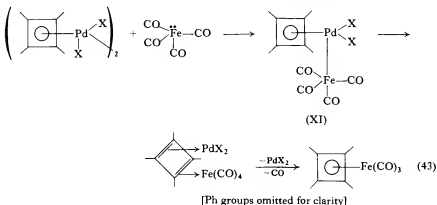
It should be noted that cyclobutadiene always replaces carbon monoxide in reactions with metal carbonyl derivatives. Yields of product parallel the known rate of exchange of CO in the starting carbonyl (184). Highest yields of ligand transfer products are attained with nickel and cobalt carbonyls which are known to very rapidly exchange their CO groups by a D-type mechanism (185–188). Lowest yields have been reported with Mo and W complexes, the carbonyls of which exchange with CO very slowly (188).

As seen from Table III, iron pentacarbonyl reacts satisfactorily in spite of its inertness towards carbon monoxide substitution under the normal conditions (189). In benzene at 80°C, however, $\text{Fe}(\text{CO})_5$ dissociates rapidly (190). The $\text{Fe}(\text{CO})_4$ generated displays a nucleophilic reactivity which should promote an A-type mechanism. In spite of the specificities discussed, Maitlis *et al.* (177) have proposed the following mechanism for the metal carbonyl exchange reactions,



according to which the reaction proceeds via free tetraphenylcyclobutadiene. The latter substitutes for carbon monoxide in $\text{Fe}(\text{CO})_5$ to give tetraphenylcyclobutadieneiron tricarbonyl. However, neither tetraphenylcyclobutadiene nor its dimer and their transformation products have been found in the mixture.

Based on the experimental data available, and drawing an analogy with π -allyl complexes, the following scheme for tetraphenylcyclobutadiene ligand transfer from palladium to iron seems more feasible.



The first step involves nucleophilic attack of $\text{Fe}(\text{CO})_4$ at the palladium atom to produce an intermediate (XI). The latter undergoes an intramolecular ligand transfer, i.e., during the reaction the tetraphenylcyclobutadiene fragment does not act as a kinetically independent particle. It is

quite probable that in the course of the transfer the ligand may convert from its π - to a π, σ -bonded state.

In summary, transfer of tetraphenylcyclobutadiene might be assumed to involve an associative mechanism of substitution with the metal increasing its coordination number in the transition state.

C. Substitution and Transfer of the π -Cyclopentadienyl Ligand

Reactivity and structure of cyclopentadienyl transition metal π -complexes have been discussed elsewhere (191–195). Many types of π -cyclopentadienyl complex are known. Replacement of the π -cyclopentadienyl ligand involves mainly bis- and mono-cyclopentadienyl derivatives. With the latter, carbonyl, halogens, π -allyl groups, etc., may serve as other ligands. The π -cyclopentadienyl group may be regarded as occupying three coordination sites. Thus bis(cyclopentadiene) derivatives may be treated as formally having the metal in an octahedral configuration. Thus in $(\pi\text{-allyl})(\pi\text{-cyclopentadienyl})\text{palladium}$, for instance, the palladium coordination number is 5; the same value could be expected for the cobalt atom in π -cyclopentadienyl-cobalt dicarbonyl. However, in $(\pi\text{-C}_5\text{H}_5)_2\text{TiX}_2$ the titanium atom is usually considered as having a formally tetrahedral configuration.

In a specific instance a substitution mechanism should take into account the individual geometry of the starting compound. It is convenient to discuss the experimental results on the $\pi\text{-C}_5\text{H}_5$ substitution and transfer reactions under three headings: (1) substitution occurring in compounds leading to increased ionic character of the metal–ligand π -bond; (2) substitution of monocyclopentadienyl compounds; (3) substitution in the ferrocene-like sandwich complexes.

1. Substitution Which Increases the Ionic Character of the Metal–Ligand π -Bond

Wilkinson *et al.* (196) were the first to discover C_5H_5 ligand transfer from one transition metal to another. Thus a number of cyclopentadienyl compounds react with FeCl_2 to give ferrocene. This is an important criterion for some ionic character in the metal–cyclopentadienyl bond. Only in solutions of the alkali metal cyclopentadienides is there a noticeable concentration of C_5H_5^- ions (197). It is questionable whether even the so-called ionic magnesium and manganese dicyclopentadienyls produce C_5H_5^- ions in solution (198). Thus it may be assumed that in all cases investigated

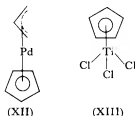
Wilkinson had observed an associative exchange of C_5H_5 rings analogous to that of $(\pi\text{-allyl})(\pi\text{-cyclopentadienyl})\text{palladium}$ and other related complexes discussed below.

The effective positive charge on the metal (199) in the compounds with enhanced ionic character of the metal-ligand bonds, together with a greater accessibility of the metal atom (200) are the reasons responsible for their fast exchange in reactions with $FeCl_2$.

2. Substitution in Monocyclopentadienyl Compounds

Covalent $\pi\text{-cyclopentadienyl}$ compounds of Ti and Pd are also capable of undergoing $\pi\text{-C}_5\text{H}_5$ ligand transfer on reaction with $FeCl_2$.

The reactivity of such compounds has been studied in detail (201-212). Substitution of the $\pi\text{-cyclopentadienyl}$ group has been investigated for monocyclopentadienyl halogen and alkoxytitanium derivatives, dicyclopentadienyltitanium halides and alkoxides (201-211), and for $(\pi\text{-allyl})(\pi\text{-cyclopentadienyl})\text{palladium}$ (212a). The stereochemistry of these complexes has been confirmed unequivocally by physical methods including X-ray studies. The structures of $(\pi\text{-allyl})(\pi\text{-cyclopentadienyl})\text{palladium}$ (213) and of $(\pi\text{-cyclopentadienyl})\text{titanium trichloride}$ (214) are shown.



The coordinative unsaturation of the palladium compound follows directly from its structure. The compound $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_3$ (coordination number 6) has a so-called "piano stool" structure and reactivity towards an electron donor molecule is probably due to the vacant nonbonding titanium orbitals (215, 216).

Nesmeyanov *et al.* (201-211) have carried out a systematic study of cyclopentadienyl ligand substitution in bis- and mono-cyclopentadienyl derivatives of titanium, including alcoholysis, hydrolysis, and reaction with $FeCl_2$.

The compounds corresponding to general formula $\text{RTi}(\text{OR}')_{3-n}\text{Hal}_n$ [where $n = 0, 1, 2, 3$; $\text{R} = \text{C}_5\text{H}_5$, MeC_5H_4 , $(\text{Me})_3\text{C}_5$; $\text{R}' = \text{Et}$, Pr-iso , Ph ; $\text{Hal} = \text{Cl}$, Br , I] as well as a series of cyclopentadienyl(trialkoxy)titaniums, with various phenyl ring substituents, have been investigated. With cyclopentadienyl(trialkoxy)titaniums, alcoholysis of the $\text{C}_5\text{H}_5\text{—Ti}$ bond proceeds almost quantitatively even at room temperature. However, it should be noted that the yield of cyclopentadiene on alcoholysis of monocyclopentadienyltitanium derivatives is determined essentially by the nature of the other ligands combined with the titanium. Thus under analogous conditions, with cyclopentadienyltitanium trihalides ring elimination does not take place (Table IV).

Some cyclopentadienyltitanium complexes react with FeCl_2 or iron acetylacetonate with transfer of the cyclopentadienyl ligand from titanium to iron. The yield of ferrocene also depends on the other ligands on titanium. The yield increases with decreasing number of electron-attractive halogen atoms in the molecule (see Table IV).

Physical methods have been employed for investigating the above-mentioned monocyclopentadienyltitanium complexes. Using NMR spectroscopy an upfield shift of the C_5H_5 protons was observed for this series with increasing yields of cyclopentadiene (on alcoholysis and hydrolysis) and ferrocenes (in reactions with FeCl_2). This may correlate with increase in the C—H bond electron density in the rings, also reflected in the IR shifts of the C—H out-of-plane bending mode.

Data on the bis(cyclopentadienyl)titanium derivatives are also listed in Table IV.

Thus in these studies it is evident that ring electron density changes occur under the action of the other ligands on the titanium. This in turn determines the degree of $\text{Ti—C}_5\text{H}_5$ bond alcoholysis and hydrolysis, and ferrocene yields in reactions with FeCl_2 .

Later the same workers carried out analogous reactions with mono- and pentamethyl-substituted cyclopentadienyl(trialkoxy)titaniums. The compound $(\pi\text{-MeC}_5\text{H}_4)\text{Ti}(\text{OEt})_3$ and FeCl_2 afforded dimethylferrocene (25%) but only under more drastic conditions (sealed tube, 150°C , 6 hours) than those employed for $(\pi\text{-C}_5\text{H}_5)\text{Ti}(\text{OEt})_3$. Under the same conditions no decamethylferrocene was obtained from $[\pi\text{-Me}_5\text{C}_5]\text{Ti}(\text{OEt})_3$ and FeCl_2 . Evidently, the presence of methyl groups in the ring markedly slows the alcoholysis, as 25 and 95%, respectively, of unreacted $(\pi\text{-C}_5\text{H}_5)\text{Ti}(\text{OEt})_3$ and $(\pi\text{-MeC}_5\text{H}_4)\text{Ti}(\text{OEt})_3$ were recovered. With

TABLE IV
SUBSTITUTION AND TRANSFER REACTION IN THE TITANIUM COMPOUNDS

Alcoholysis				C ₃ H ₅ transfer to Fe			NMR data		IR spectral data	
Reaction temperature (°C)	% C ₃ H ₆ Yield	References	Reagent	Reaction conditions ^a	% Ferrocene yield	References	C ₃ H ₅	References	Out-of-plane bending mode C ₃ H ₅ (cm ⁻¹)	References
(π -C ₃ H ₅)TiCl ₃	80	0	201, 207	—	—	—	7.21	206, 207	838	209
(π -C ₃ H ₅)Ti(OC ₂ H ₅)Cl ₂	80	Traces	203, 207	Fe(C ₃ H ₇ O ₂) ₂	THF, 150°, 8 hr	Traces	6.79	206, 207	835	209
(π -C ₃ H ₅)Ti(OC ₂ H ₅) ₂ Cl	80	19	203, 207	Fe(C ₃ H ₇ O ₂) ₂	THF, 150°, 8 hr	9	6.40	206, 207	815	209
(π -C ₃ H ₅)Ti(OC ₂ H ₅) ₃	80	100	201, 203	FeCl ₂	THF, 65°, 1 hr	70	6.22	206, 207	806	209
	20	77	207	FeCl ₂	THF, 65°, 15 min	70	—	206	—	—
				FeCl ₃	MeNO ₂ , 100°, 1 hr	74	—	207	—	—
				Fe(C ₃ H ₇ O ₂) ₂	N ₂ , 65°, 1 hr	—	—	—	—	—
(π -C ₃ H ₅)TiBr ₃	80	18	207	Fe(C ₃ H ₇ O ₂) ₂	THF, 150°, 8 hr	Traces	6.67	207	829	208
(π -C ₃ H ₅)Ti(OC ₂ H ₅)Br ₂	80	10	207	Fe(C ₃ H ₇ O ₂) ₂	—	—	6.84	207	833	208
(π -C ₃ H ₅)Ti(OC ₂ H ₅) ₂ Br	80	31	207	Fe(C ₃ H ₇ O ₂) ₂	150°, 8 hr	9	6.47	207	811	208
(π -C ₃ H ₅)TiI ₃	80	6	207	Fe(C ₃ H ₇ O ₂) ₂	—	—	7.05	—	828	208
(π -C ₃ H ₅)Ti(OC ₂ H ₅)I ₂	80	14	207	Fe(C ₃ H ₇ O ₂) ₂	—	—	6.76	207	817	208
(π -C ₃ H ₅)Ti(OC ₂ H ₅) ₂ I	80	25	207	Fe(C ₃ H ₇ O ₂) ₂	THF, 150°, 3 hr	11	6.42	207	817	208
(π -C ₃ H ₅)Ti(OC ₃ H ₇ -iso)Cl ₂	80	15	207	Fe(C ₃ H ₇ O ₂) ₂	THF, 150°, 3 hr	4	6.59	207	817	208
(π -C ₃ H ₅)Ti(OC ₃ H ₇ -iso) ₂ Cl	80	47	207	Fe(C ₃ H ₇ O ₂) ₂	THF, 150°, 3 hr	11	6.35	207	817	208

$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OC}_4\text{H}_9\text{-}i\text{tert})_3$	80	76	203	$\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2$	THF, 65°, 1 hr	56	206	6.25	206	805	209
$(\pi\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti}(\text{OC}_2\text{H}_5)_3$	20	5	203	FeCl_2	THF, 150°, 1 hr	25	210	5.98	206–207	801	209
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OCOCH}_3)_3$	80	68	203	FeCl_2	THF, 65°, 1 hr	55	206	6.43	206	807	209
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}[(\text{OC}_5\text{H}_9(\text{CH}_3)_2\text{-}3,5)]_3$	20	57	211	—	—	—	—	6.48	211	—	209
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}p)_3$	80	91	211	—	—	—	—	6.50	211	—	209
	20	58	211								
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OC}_6\text{H}_5)_3$	80	76	211	$\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2$	THF, 65°, 1 hr	51	206	6.54	211	—	209
	20	37	211								
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OC}_6\text{H}_4\text{Cl-}o)_3$	80	83	211	—	—	—	—	6.39	211	—	209
	20	Traces	211								
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OC}_6\text{H}_4\text{F-}p)_3$	80	78	211	—	—	—	—	6.49	211	—	209
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OC}_6\text{H}_4\text{NO}_2\text{-}p)_3$	80	43	211	—	—	—	—	6.54	211	—	209
	20	0	211								
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{ONC}_9\text{H}_6)_2$	90	86	204	—	—	—	—	6.26	211	—	209
$(\text{OC}_2\text{H}_5)(\text{C}_2\text{H}_5\text{OH})$											
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OCOCCH}_3)_2$	80	63	203	FeCl_2	THF, 65°, 1 hr	46	205, 206	6.5	206	822–832	209
	20	42	203	FeCl_2	MeNO_3 , 100 hr	44	206	—	183, 206		
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OCOC}_2\text{H}_5)_2$	80	75	203	FeCl_2	THF, 65°, 1 hr	36	206	6.49	206	815–831	209
	20	53	203	FeCl_2	THF, 65°, 1 hr	—	206				
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}$	—	—	—	FeCl_2	THF, 65°, 1 hr	4	206	—	—	—	—
				$\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2$	THF, 65°, 1 hr	4	206				
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OCOCCH}_2\text{Cl})_2$	80	71	208	—	—	—	—	—	—	835–845	209
	20	24	208								
$(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2$	80	Traces	202	—	—	—	—	—	—	822	209

* Temperatures, °C.

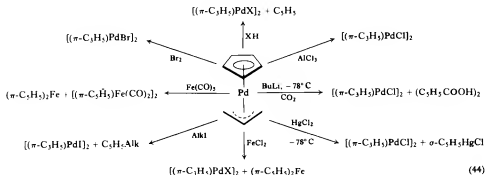
$(\pi\text{-Me}_5\text{C}_5)\text{Ti}(\text{OEt})_3$ the ring does not cleave in ethanol. It can be eliminated only by heating with sodium ethoxide in ethanol (sealed tube, 150°C , 6 hours) giving $\text{Me}_5\text{C}_5\text{H}$ in 55% yield.

Thus electron-releasing substituents on the $\pi\text{-C}_5$ ring decrease reactivity in these reactions.

Apparently for alcoholysis, hydrolysis, and reaction with FeCl_2 , a vacant metal orbital and an effective positive charge on titanium are the motive forces for nucleophilic exchange of the rings (216). Methyl groups decrease the positive charge. Moreover the five methyl groups may sterically hinder attack of a reagent on the titanium atom. Both of these factors diminish reactivity of the respective methyl-substituted derivatives with respect to the unsubstituted ones.

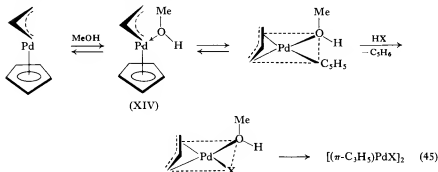
Probably substitution of the cyclopentadienyl ligand on alcoholysis and hydrolysis, and its transfer in reactions of di- and monocyclopentadienyl-titanium derivatives with FeCl_2 or iron(II) acetylacetonate, follows a mechanism common for π -ligand exchange in other metal π -complexes (see later).

Other characteristic examples of easy substitution of the $\pi\text{-C}_5\text{H}_5$ ring in coordinatively unsaturated complexes include cleavage and transfer of the π -cyclopentadienyl ligand in $(\pi\text{-allyl})(\pi\text{-cyclopentadienyl})\text{palladium}$ (212):



The reactions are very fast, and halide ion addition always leads to π -allylpalladium halide dimers. The cyclopentadienyl moiety has been isolated in the form of cyclopentadiene (reaction with hydrogen chloride), or as a carboxylic acid dimer (reaction with $\text{BuLi} + \text{CO}_2$). That part of the attacking reagent bearing positive charge always combines with the C_5H_5 ,

group. If the metal is able to form cyclopentadienyl derivatives, then reaction with one of its salts affords a product involving cyclopentadienyl transfer from palladium to this metal. For example, ferrous chloride gives ferrocene, and mercury salts produce the respective mercury derivatives. Reaction of $(\pi\text{-allyl})(\pi\text{-cyclopentadienyl})$ palladium with iron carbonyl gives cyclopentadienyliron dicarbonyl dimer and ferrocene. The authors have proposed the mechanism shown for cyclopentadienyl ligand substitution in $(\pi\text{-allyl})(\pi\text{-cyclopentadienyl})$ palladium (212).

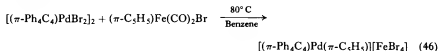


Initially a solvent molecule attacks a vacant coordination site on Pd in $(\pi\text{-C}_5\text{H}_5)_2\text{Pd}(\pi\text{-C}_5\text{H}_5)$ to give a 20-electron intermediate (XIV) having a distorted square-planar configuration. Probably the latter then becomes stabilized by the $\pi\text{-C}_5\text{H}_5\text{Pd}$ bond changing to a localized σ -bond. Subsequent reactions proceed as ordinary ligand substitution in square-planar complexes (1).

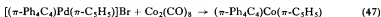
Such a scheme has been proposed based on the UV spectrum and polarogram of $(\pi\text{-allyl})(\pi\text{-cyclopentadienyl})$ palladium (212). A complete X-ray study of this compound carried out by Struchkov *et al.* (213) revealed that the palladium atom has a vacant coordination site. In essence, the scheme proposed is a version of associative substitution via change in ligand bond character in the transition state.

Based on the results obtained, the following general scheme is proposed by the present authors for the π -ligand substitution in the transition metal π -complexes. This involves three main steps. At first coordination of the attacking agent occurs, then the π -delocalized ligand transfers to its σ -bonded state or to some intermediate state, involving a lowering of the coordinative demands of the ligand. Finally, ligand removal proceeds via so-called cis insertion.

Special attention should be paid to Maitlis's study of the π -cyclopentadienyl ligand transfer from iron to other metals in reactions of $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ and $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ with various compounds. In 1964 Maitlis, Efraty, and Games found (179) that $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ or $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ react in boiling benzene with (tetraphenylcyclobutadiene) palladium bromide:

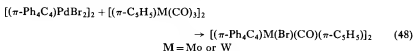


In the same manner tetraphenylcyclobutadiene complexes of nickel and cobalt gave $[(\pi\text{-Ph}_4\text{C}_4)\text{Ni}(\pi\text{-C}_5\text{H}_5)]\text{FeBr}_4$ and $[(\pi\text{-Ph}_4\text{C}_4)\text{Co}(\pi\text{-C}_5\text{H}_5)]$, respectively (179). Titanium tetrachloride and iron pentacarbonyl also react with $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ to give $(\pi\text{-cyclopentadienyl})\text{titanium trichloride}$ and ferrocene (179). A complex of palladium bromide with cycloocta-1,5-diene reacts with $(\pi\text{-cyclopentadienyl})\text{iron dicarbonyl iodide}$ to give $[(\pi\text{-1,5-COD})\text{Pd}(\pi\text{-C}_5\text{H}_5)]\text{FeBr}_4$, isolated as tetrabromoferrate or bromide (179); $(\pi\text{-tetraphenylcyclobutadiene})(\pi\text{-cyclopentadienyl})\text{palladium bromide}$ may itself be employed as a cyclopentadienylating agent (181).

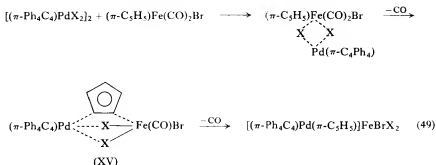


As seen from this scheme, the reaction involves transfer of the tetraphenylcyclobutadiene ligand as well.

The cyclopentadienyl tricarbonyl molybdenum and tungsten dimers also react with $[(\pi\text{-Ph}_4\text{C}_4)\text{PdX}_2]_2$ ($\text{X} = \text{Cl}, \text{Br}$) complexes but by transfer of the tetraphenylcyclobutadiene group (182).



Attempts to extend this reaction to cyclopentadienyltitanium dichloride were unsuccessful (179). The authors have failed to isolate nickelocene in the reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ with nickel carbonyl (179). Thus only the iron complexes $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ and $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Br}$, which according to Basolo *et al.* are practically unable to substitute carbonyl groups (188), can act as cyclopentadienylating agents. Maitlis has proposed the following scheme for reaction of tetraphenylcyclobutadienepalladium dihalides with $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ (180):



Thus the iron atom in $(\pi\text{-cyclopentadienyl})\text{iron dicarbonyl bromide}$ forms additional bonds with the halide ligands on palladium. Carbonyl substitution on the generated intermediate (XV) then occurs. In this case the cyclopentadienyl group acts as a bridge. In general, such a mechanism corresponds to an A-type substitution, where the halogens in $(\pi\text{-tetraphenylcyclobutadiene})\text{palladium dichloride}$ function as nucleophiles.

It is hard to believe, however, that a coordinatively and electronically saturated iron atom in $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ can associate with nucleophiles via additional bridge bonds. Besides which it is known that halogen is not active under conditions of $\text{S}_{\text{N}}2$ substitution (217). Probably the first step of reaction (49) involves dissociation (either CO and Br may be eliminated), so that a generated intermediate then reacts with a substrate. As a result the ligand transfer via an intermediate does not differ from other mechanisms proposed.

It is interesting to compare the reaction schemes for the titanium derivatives with these proposed for cyclopentadienyliron dicarbonyls. In both cases C_5H_5 transfer occurs. In the former case the electron-deficient compound is the substrate, in the latter case the substrate is the electron donor. Thus ligand transfer from the titanium is a nucleophilic substitution, whereas the similar reaction for the iron derivatives can be described in terms of electrophilic substitution. The latter conclusion is in agreement with the results of Cramer (85), who has suggested that CO substitution by halogens in the above-mentioned iron complexes follows an electrophilic mechanism (218, 219).

Thus in π -ligand substitution a change in metal coordination number rather than direction of electron density shift in the transition state is quite significant.

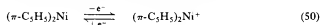
3. Substitution in Ferrocene-like Sandwich Complexes

Analogous factors operate for substitution and transfer of π -C₅H₅ rings in the ferrocene-type compounds. It should be pointed out that among dicyclopentadienyls of Group VIII transition metals only nickelocene readily reacts in this manner. Among the numerous reactions of the ferrocene ring, substitution and exchange processes are so few that in the available reviews they are usually the least discussed. Differences between $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}$ and $(\pi\text{-C}_5\text{H}_5)_2\text{Fe}$ are, of course, related to their different electronic structures. Earlier it has been noted that in π -ligand substitution the coordination number of the metal usually increases in the transition state. In ferrocene and its analogs neither geometry nor electronic structure provide an additional coordination site for the metal. In contrast nickelocene is a 20-electron complex with two unpaired electrons in the doubly degenerate e_{2g}^* levels. Such a configuration is essentially unstable. As seen from Table V, nickelocene readily undergoes substitution or transformation reactions involving one of its C₅H₅ ligands, giving rise to stable 18-electron systems. This tendency is independent of the nature of the attacking agent. Both nucleophilic and electrophilic reagents produce 18-electron complexes.

A study of these reactions faces two problems: site of attack by the reagent, and which of nickelocene's properties (electron-releasing or electron-withdrawing) are predominant during formation of the intermediate, which in most cases has an uncertain structure.

It has been shown (220) that the highest half-occupied MO's are those of the e_{2g} symmetry in which the nickel AO and C₅H₅ MO's contribute almost equally. Thus it can be concluded that nickelocene possesses stronger donor and acceptor properties than does ferrocene.

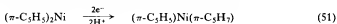
Let us consider the redox properties of nickelocene (221). A polarogram of $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}$ shows anodic ($E_{1/2} = -0.08$ V) and irreversible cathodic waves ($E_{1/2} = -1.78$ V). The first wave corresponds to the one-electron reversible oxidation of nickelocene to its uncharged cation.¹⁰



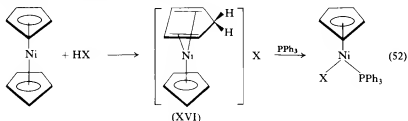
This reaction is easier by 0.4 V than ferrocene oxidation. It might be assumed that analogously with other metallocenes, the electron charges in

¹⁰ The second oxidation stage of $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}$, giving rise to $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}^{2+}$, can be observed at the Pt electrode at +0.77 V (212a).

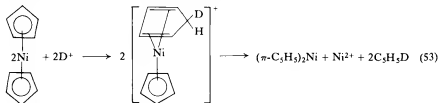
nickelocene are localized at the metal atom during oxidation. The second cathodic wave corresponds to a two-electron, two-proton reduction of nickelocene to $(\pi\text{-C}_5\text{H}_5)(\pi\text{-cyclopentadienyl})\text{nickel}$.



Analogous products are generated in the chemical reduction of nickelocene with sodium amalgam (222). Based on these data it might be concluded that for nickelocene the electron changes are localized on the $\pi\text{-C}_5\text{H}_5$ ligands during reduction. This conclusion agrees with such chemical properties of nickelocene as its activity in reactions with dienophiles (maleic anhydride, acetylenedicarboxylic acid) (223). An interesting scheme has been proposed by Van der Akker (224) for the reaction









The reaction has been found to demand a proton for its occurrence and it does not proceed with RX instead of HX . It has been assumed that the first step involves electrophilic attack of HX at the cyclopentadienyl group and formation of the unstable protonated complex (XVI) from which replacement of cyclopentadiene and formation of the final product can occur.¹¹ Cyclopentadiene has been identified by GLC. Probably the second stage involves preliminary coordination of PPh_3 with the nickel atom. Observation of Setkina and Kursanov, (226) corroborate the Van der Akker mechanism. They have found that in reactions with deuterated acids, unreacted nickelocene contains no deuterium in its five-membered rings. Probably the following reaction takes place in acidic media



¹¹ For an alternative viewpoint on the mechanism of this reaction see Ustynyuk (225).






TABLE V. SUBSTITUTION AND TRANSFER OF THE π -CYCLOPENTADIENYL LIGAND


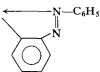
Reaction	Reaction conditions ^a	Yield %	References
$(\pi\text{-C}_5\text{H}_5)_2\text{V} + \text{CO} \rightarrow (\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$	—	—	262, 263
$(\pi\text{-C}_5\text{H}_5)_2\text{ZrCl}_2 + \text{RCOOH} \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Zr}(\text{OCOR})_3$ R = CH ₃ C ₄ H ₉ C ₈ H ₁₇	CH ₃ COOH, 105°, 9 hr CH ₃ COOH, 5 hr C ₈ H ₁₇ COOH, 100°, 11 hr	66 87 85	264
CF ₃	CF ₃ COOH, 70°, 1.5 hr	0	
$(\pi\text{-C}_5\text{H}_5)\text{Zr}(\text{OCOCH}_3)_3 + \text{C}_5\text{H}_8\text{O}_2 \rightarrow (\text{C}_5\text{H}_7\text{O}_2)_4\text{Zr}$	C ₅ H ₈ O ₂ , 80°, 5 hr	54	264
$(\pi\text{-C}_5\text{H}_5)_2\text{ZrCl}_2 + \text{RCOCH}_2\text{COR} \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Zr}(\text{Cl})$ 	R = CH ₃ C ₆ H ₅ C ₅ H ₈ O ₂ , 80°, 2 hr Benzene, 100°, 15 hr	95 69	265
$(\pi\text{-C}_5\text{H}_5)_2\text{ZrX}_2 + \text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4 \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Zr}(\text{Cl})(\text{C}_5\text{H}_7\text{O}_2)_2$ X = Cl Br	Toluene, 120°, 3 hr	19 39	266
$(\pi\text{-C}_5\text{H}_5)_4\text{Zr} + \text{H}_2\text{O} \xrightarrow{\text{TIOH}} \text{C}_5\text{H}_5\text{Ti} + \text{ZrO}_2$	100°, 2.5 hr	71	267
$(\pi\text{-C}_5\text{H}_5)_4\text{Zr} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{TIOH}} \text{C}_5\text{H}_5\text{Ti} + \text{Zr}(\text{OC}_2\text{H}_5)_4$	95°, 2 hr	86	
$(\pi\text{-C}_5\text{H}_5)_4\text{Zr} + \text{HNO}_3 \rightarrow (\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{ONO}_2)_2$	C ₂ H ₄ Cl ₂ , -35°, 2 hr	67	
$(\pi\text{-C}_5\text{H}_5)_4\text{Zr} + \text{C}_6\text{H}_5\text{COOH} \rightarrow [(\pi\text{-C}_5\text{H}_5)\text{Zr}(\text{OCOC}_6\text{H}_5)]_2\text{O}$	THF, -10°, 2 hr	45	
$(\pi\text{-C}_5\text{H}_5)_4\text{Zr} + \text{ZrCl}_4 \rightarrow (\pi\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$	THF, 40°, 6 hr	34	267
$(\pi\text{-C}_5\text{H}_5)_4\text{Zr} + \text{R}'\text{COCH}_2\text{COR} \rightarrow (\pi\text{-C}_5\text{H}_5)_2\text{Zr}$ 	R' = R'' = CH ₃ R' = R'' = C ₆ H ₅ R' = CH ₃ , R'' = C ₆ H ₅ Benzene, 20°, 2 hr Benzene, 80°, 15 min Benzene, 20°, 2 hr	100 63 52	267

$(\pi\text{-C}_5\text{H}_5)_2\text{ZrCl}_2 + $  $\longrightarrow (\pi\text{-C}_5\text{H}_5)_2\text{Zr} \left(\text{Naphthyl-O} \right)_3$	Benzene, 80°, 20 min	51	268
$(\pi\text{-C}_5\text{H}_5)_2\text{ZrC}_5\text{H}_7\text{O}_2 + $  $\longrightarrow (\pi\text{-C}_5\text{H}_5)_2\text{Zr} \left(\text{Naphthyl-O} \right)_3$	Benzene, 80°, 15 min	90	
$(\pi\text{-C}_5\text{H}_5)_4\text{Zr} + $  $\longrightarrow (\pi\text{-C}_5\text{H}_5)_2\text{Zr} \left(\text{Naphthyl-O} \right)_3$	Benzene, 100°, 1.5 hr	68	
$(\pi\text{-C}_5\text{H}_5)_2\text{HfCl}_2 + \text{C}_5\text{H}_7\text{O}_2 \rightarrow (\pi\text{-C}_5\text{H}_5)_2\text{Hf}(\text{Cl})(\text{C}_5\text{H}_7\text{O}_2)_2$	$\text{C}_5\text{H}_8\text{O}_2$, 40°, 25 min	59	269
$(\pi\text{-C}_5\text{H}_5)_2\text{HfCl}_2 + $  $\longrightarrow (\pi\text{-C}_5\text{H}_5)_2\text{Hf} \left(\text{Naphthyl-O} \right)_3$	Benzene, 80°, 10 min	58	269
$(\pi\text{-C}_5\text{H}_5)_4\text{Hf} + \text{KOH} \xrightarrow{\text{TlOH}} \text{C}_5\text{H}_5\text{Tl}$	105°, 3 hr	81	269
$(\pi\text{-C}_5\text{H}_5)_4\text{Hf} + \text{HCl} \rightarrow (\text{C}_5\text{H}_5)_2\text{HfCl}_2$	20°, 15 min	57	269

(Continued)

TABLE V—continued

Reaction	Reaction conditions*	% Yield	References
$(\pi\text{-C}_5\text{H}_5)_4\text{Hf} + \text{HNO}_3 \rightarrow (\pi\text{-C}_5\text{H}_5)_2\text{Hf}(\text{ONO}_2)_2$	25°, 2 hr	38	269
$(\pi\text{-C}_5\text{H}_5)_4\text{Hf} + $  $ \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Hf} \left(\text{Naphthyl-O} \right)_3$	Benzene, 80°, 1 hr	34	269
$(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4 + \text{Erythroporphin}$	—	—	270
$(\pi\text{-C}_5\text{H}_5)_2\text{Cr} + \text{FeCl}_2 \rightarrow (\pi\text{-C}_5\text{H}_5)_2\text{Fe}$	THF, 65°, 6 hr	10	196
$(\pi\text{-C}_5\text{H}_5)_2\text{Cr} + \text{CO} \rightarrow (\pi\text{-C}_5\text{H}_5)_3\text{Cr}_2(\text{CO})_3$	100 atm, 100°	—	271, 272
$(\pi\text{-C}_5\text{H}_5)_2\text{Cr} + \text{CO} \rightarrow \text{Cr}(\text{CO})_6$	100 atm, 250°	—	271, 272
$(\pi\text{-C}_5\text{H}_5)_2\text{Cr} + \text{CO} \rightarrow [(\pi\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$	100 atm, 170°	—	271, 272
$(\pi\text{-C}_5\text{H}_5)_2\text{Co} + \text{CO} \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$	200 atm, 150°	—	273, 274
$(\pi\text{-C}_5\text{H}_5)_2\text{Co} + \text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5 \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Co} \left(\text{Ph-N} \right)_2$ 	160°, 3 hr, N ₂	39	275
$(\pi\text{-C}_5\text{H}_5)_2\text{Co} + \text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_4\text{-CH}_3\text{-}m \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Co} \left(\text{Ph-N} \right)_2$ 	160°, 3.5 hr, N ₂	13	275
$(\pi\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2 + \text{C}_6\text{H}_5\text{-NH-}$  $ \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Co} \left(\text{Ph-NH} \right)_2$ 	160°, 1 hr, N ₂	0.6	275

$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Ni}$ 	THF, 95°, 24 hr	9.5	276
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{C}_3\text{H}_5\text{MgCl} \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Ni}(\pi\text{-C}_5\text{H}_5)$	THF, 24 hr, 0°		
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{PhC}\equiv\text{CPh} + \text{Fe}(\text{CO})_5 \rightarrow [(\pi\text{-C}_5\text{H}_5)_2\text{Ni}][(\text{C}_6\text{H}_5)_2\text{C}_2][\text{Fe}(\text{CO})_3]$ (XXII)	Benzene, 80°, 22 hr	50 12	277
$\quad\quad\quad + [(\pi\text{-C}_5\text{H}_5)_2\text{Ni}][(\text{C}_6\text{H}_5)_2\text{C}_2][\text{Fe}_2(\text{CO})_6]$ (XXIII)	N ₂	5	
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{PhC}\equiv\text{CPh} \rightarrow [(\pi\text{-C}_5\text{H}_5)_2\text{Ni}]_2(\text{C}_6\text{H}_5)_2\text{C}_2$ (XX)	Benzene, 80°, 6 hr	85	
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{Fe}(\text{CO})_5 \rightarrow [(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2 + [(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})_2\text{Fe}(\text{CO})\text{C}_5\text{H}_5] + [(\pi\text{-C}_5\text{H}_5)\text{NiCO}]_2$	Benzene, 80°, N ₂ , 8 hr	— traces	236–239
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{Ni}(\text{CO})_4 \rightarrow (\pi\text{-C}_5\text{H}_5)_2\text{NiCO} + (\pi\text{-C}_5\text{H}_5)_3\text{Ni}(\text{CO})_2$	Benzene, 70°, 12 hr, N ₂	50 40	240
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{Ni}(\text{CO})_4 \rightarrow [(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$	Benzene, 80°, 3.5 hr, N ₂	74	
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{C}_6\text{H}_{11}\text{NC} \rightarrow [(\pi\text{-C}_5\text{H}_5)\text{NiCNC}_6\text{H}_{11}]_2$	25°	38	245
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + (\text{CNC}_6\text{H}_5)_4\text{Ni} \rightarrow [(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CNC}_6\text{H}_5)]_2$	Benzene	80	246
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{RSH} \rightarrow [(\pi\text{-C}_5\text{H}_5)\text{NiSR}]_2$ R = C ₆ H ₅ C ₂ H ₅ CH ₃	Benzene, 25°, 15 hr	95 96 67	243, 244
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5 \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Ni}$ 	135°, 4 hr, N ₂	25	230
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{NO} \rightarrow (\pi\text{-C}_5\text{H}_5)\text{NiNO}$	Petroleum ether, 90°–110°	—	278, 279
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{L}_2\text{NiX}_2 \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{L})\text{X}$ L = P(C ₆ H ₅) ₃ X = Cl P(C ₆ H ₅) ₃ Cl P(C ₆ H ₅) ₂ Me Br	THF, 25°, 0.5 hr	90 67 79	280

(Continued)

TABLE V—continued

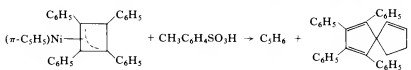
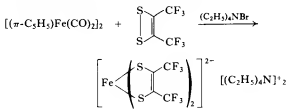
Reaction	Reaction conditions ^a	% Yield	References
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{L} \xrightarrow[\text{I}_2]{\text{Ni(CO)}_4} (\pi\text{-C}_5\text{H}_5)\text{Ni(I)L}$ $\text{L} = \text{P(OC}_6\text{H}_5)_3$ $\text{As(C}_6\text{H}_5)_3$ $\text{Sb(C}_6\text{H}_5)_3$	THF, 25°, 0.5 hr	39 53 52	280
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{NiBr}_2 + \text{As(C}_6\text{H}_5)_3 \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Ni(Br)[(C}_6\text{H}_5)_3\text{As}]$	THF, 25°, 0.5 hr	66	280
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + [(\text{C}_6\text{H}_5)_3\text{PH}]\text{Cl} \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Ni}[(\text{C}_6\text{H}_5)_3\text{P}]\text{X}$ $\text{X} = \text{Cl}$ Br I F	Ether, 25°, 4 hr	67 60 56 —	224
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{P(C}_6\text{H}_5)_3 + \text{XY} \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Ni}[(\text{C}_6\text{H}_5)_3\text{P}]\text{Hal}$ $\text{Y} = \text{H} \quad \text{X} = \text{Halogen}$ CCl_3 CHBr_2	Benzene, 10°, 15 min Benzene, 0°, 2.5 hr CCl_4 , 20 min, 81° Ether, 2 hr, 35°	88 32 89 42	225
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{P(OC}_6\text{H}_5)_3 + \text{CCl}_4 \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Ni}[(\text{C}_6\text{H}_5\text{O})_3\text{P}]\text{Cl}$	CCl_4 , 80°, 20 min	89	225
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{Li}^+[\text{C}_5\text{H}_4\text{CH(C}_6\text{H}_5)\text{N(CH}_3)_2]^- \rightarrow [(\text{CH}_3)_2\text{N}-\underset{\text{C}_6\text{H}_5}{\text{CH}}-\text{C}_5\text{H}_4]_2\text{Ni}$	Ether, 25°, 30 min	30	225
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{L} \xrightarrow{\text{HCl}} \text{L}_2\text{NiCl}_2$ $\text{L} = \text{dipy}$ phen	Ether, 35°, 1.5 hr CCl_4	96 59	225
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{L} \xrightarrow{\text{HCl}} \text{L}_4\text{NiCl}_2$ $\text{L} = \text{C}_5\text{H}_5\text{N}$ $\text{C}_6\text{H}_5\text{NH}_2$	py, 80°, 20 min CCl_4 , 80°, 1 hr	85 90	225
$p\text{-CH}_3\text{-C}_6\text{H}_4\text{-N} \rightarrow \text{O}$	THF, 65°, 1 hr	—	

$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{L} \rightarrow \text{L}_2\text{Ni}$	
L = Dimethylglyoxime	
Diazoaminobenzene	
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + (\text{CH}_3)_2\text{SO} \rightarrow \{[(\text{CH}_3)_2\text{SO}]_6\text{Ni}\}\text{NiCl}_4$	
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{C}_6\text{H}_5\text{NC} \rightarrow [(\text{C}_6\text{H}_5)\text{NC}]_4\text{Ni}$	
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + (\text{C}_6\text{H}_5)_3\text{P} \rightarrow [(\text{C}_6\text{H}_5)_3\text{P}]_4\text{Ni}$	
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{PF}_3 \rightarrow (\text{PF}_3)_4\text{Ni}$	
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{NH}_3 \rightarrow [\text{Ni}(\text{NH}_3)_6](\text{C}_5\text{H}_5)_2$	
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{KCN} \rightarrow \text{K}_2[\text{Ni}(\text{CN})_4]$	
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni} + \text{L} \rightarrow \text{L}_4\text{Ni}$	
L = $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{C}_6\text{H}_5\text{NC}$, 1,2-bis(diphenylphosphino)ethane,	
1,1,1-tris(diphenylphosphinomethyl)ethane	
$(\pi\text{-C}_5\text{H}_5)\text{Pd}(\pi\text{-C}_6\text{H}_6) + \text{L} \rightarrow \text{PdLx}$	
L = $\text{C}_6\text{H}_5\text{NC}$; x = 2	
iso- $\text{C}_3\text{H}_7\text{NC}$; x = 2	
$\text{P}(\text{C}_6\text{H}_5)_3$; x = 2	
$\text{P}(\text{C}_6\text{H}_5)_3$; x = 4	
$(\pi\text{-C}_5\text{H}_5)\text{Pd}(\pi\text{-C}_3\text{H}_3) + \text{HCl} \rightarrow \text{C}_5\text{H}_6 + [(\pi\text{-C}_3\text{H}_3)\text{PdCl}]_2$	
+ $\text{FeCl}_2 \rightarrow (\text{C}_5\text{H}_5)_2\text{Fe} + [(\pi\text{-C}_3\text{H}_3)\text{PdCl}]_2$	
+ $\text{Fe}(\text{CO})_5 \rightarrow (\text{C}_5\text{H}_5)_2\text{Fe} + [(\pi\text{-C}_3\text{H}_3)\text{PdCl}]_2$	
+ $(\text{C}_5\text{H}_5)_2\text{Fe}(\text{CO})_4$	
+ $\text{HgCl}_2 \rightarrow \text{C}_5\text{H}_5\text{HgCl} + [(\pi\text{-C}_3\text{H}_3)\text{PdCl}]_2$	
$(\pi\text{-C}_5\text{H}_5)\text{Pt}(\text{CH}_3)_3 + \text{NBS} \rightarrow \text{C}_5\text{Br}_6 + (\text{CH}_3)_3\text{PtBr}$	
$(\pi\text{-C}_5\text{H}_5)_2\text{Fe} + (\text{C}_6\text{H}_5\text{COO})_2 \rightarrow \text{Fe}(\text{OCOC}_6\text{H}_5)_3$	
$(\pi\text{-C}_5\text{H}_5)_2\text{Fe} + o\text{-C}_6\text{H}_4(\text{CN})_2 \rightarrow \text{Iron phthalocyanine}$	
$(\pi\text{-RC}_5\text{H}_4)_2\text{Fe} + \text{Ar} \xrightarrow{\text{AlCl}_3} (\pi\text{-C}_5\text{H}_5)\text{Fe}(\pi\text{-Ar})\text{AlCl}_4$	
R = C_2H_5 Ar = C_6H_6	
C_2H_5 $(\text{CH}_3)_3\text{C}_6\text{H}_3$	
CH_3CO $(\text{CH}_3)_3\text{C}_6\text{H}_3$	
C_6H_5 C_6H_5	

Ethanol, 25°	97	225
Xylene, 30°, 15 hr	86	
80°, CCl_4	87	225
—	—	281
Benzene, 80°	100	282
Under PF_3 pressure,	95	283
60°, 96 hr		
Liquid NH_3 , -20°	—	281
Liquid NH_3 , -20°	—	—
Cyclohexane, 120°	100	225
—	—	225
Ether, 0°, 2	90	
Ether, -10°	73	
Pentane, 25°	92	
CH_3OH , 25°	80	284
THF, 4 hr, 65°	65	
Benzene, 25°	—	
Ethanol, -78°	30	
CCl_4 , 80°, 1 hr	80	284
Benzene, 80°, 7 hr	100	285
Trichlorobenzene,	55	286
refluxing, 8 hr		
		255-260
Benzene, 80°, 8 hr	20	
Mesitylene, 130°, 5 hr	32	
Mesitylene, 130°, 5 hr	22	
Benzene, 80°, 8 hr	82	

(Continued)

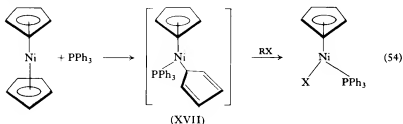
TABLE V—continued

Reaction	Reaction conditions *	% Yield	References
 $(\pi\text{-C}_5\text{H}_5)\text{Ni} + \text{C}_4\text{H}_4(\text{C}_6\text{H}_5)_2 \rightarrow \text{C}_3\text{H}_6 + \text{C}_{10}\text{H}_8(\text{C}_6\text{H}_5)_2$	Benzene, 40°, 1 hr	34	287, 288
$(\pi\text{-C}_5\text{H}_5)\text{Ni}(\pi\text{-C}_3\text{H}_5) + \text{HCl} \rightarrow \text{C}_3\text{H}_6 + [(\pi\text{-C}_3\text{H}_5)\text{NiCl}]_2$	Ethanol, 25°	26	284
$(\pi\text{-C}_5\text{H}_5)_2\text{Fe} + \text{RuCl}_3 \rightarrow (\pi\text{-C}_5\text{H}_5)_2\text{Ru}$	250°	42	289
 $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2 + \text{S}_2\text{C}(\text{CF}_3)_2 \xrightarrow{(\text{C}_2\text{H}_5)_4\text{NBr}} \left[\text{Fe} \left(\text{C}_2\text{H}_4 \right) \left(\text{S}(\text{CF}_3)_2 \right)_2 \right]^{2-} + [(\text{C}_2\text{H}_5)_4\text{N}]^{+}_2$	Benzene, UV irradiation, 8.5 40 hr		290

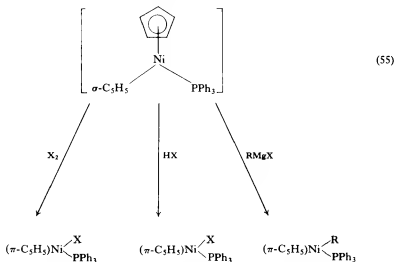
* Temperatures, °C.

Thus it is quite obvious that the resulting nickelocene cannot contain deuterium.

Another mechanism for the reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}$ with triphenylphosphine in halogen-containing solvents has been advanced by Ustynyuk (225). In his opinion nucleophilic PPh_3 attack at the nickel and formation of the σ -cyclopentadienyl complex (XVII) in a transition state take place.



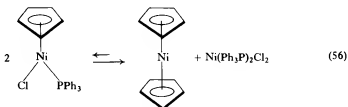
Attempts were made to isolate complex (XVII). However, only indirect proof of its formation could be obtained (227).



Treatment of the reaction mixture (PPh_3 + nickelocene) with mercuric chloride (a soft reagent cleaving metal-carbon σ -bonds) gave no $\sigma\text{-C}_5\text{H}_5\text{HgCl}$. Nickelocene and triphenylphosphine-mercuric chloride complexes have always been the reaction products (228).

These results indicate that nickelocene and triphenylphosphine afford an unstable weak complex whose subsequent transformation is defined by the activity of the attacking reagent. Experience shows that the half-sandwiches having the $\text{Ni}(\pi\text{-C}_5\text{H}_5)$ group may readily disproportionate to nickelocene.

This is also evident from the polarographic study of Gubin and Smirnova (229) carried out for the $(\pi\text{-C}_5\text{H}_5)_2\text{Ni-PPh}_3$ system. In the absence of a halogen source reduction is analogous to those of nickelocene and triphenylphosphine reduced separately under the same conditions. However, when dissolved in acetonitrile $(\pi\text{-C}_5\text{H}_5)\text{Ni(PPh}_3\text{)Cl}$ undergoes a disproportionation (229).

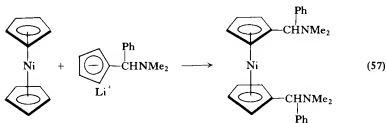


Probably the reaction involves an intermediate with $\pi\text{-C}_5\text{H}_5$ ligand transfer, but its mechanism is as yet uncertain.

Substitution of both cyclopentadienyl ligands in nickelocene proceeds easily with mono- or bidentate ligands. With monodentate ligands tetrahedral complexes $\text{Ni}(0)$ are formed, while with bidentate ligands (such as α, α' -dipyridyl, 1,10-phenanthroline, etc.) square-planar complexes are produced (225).

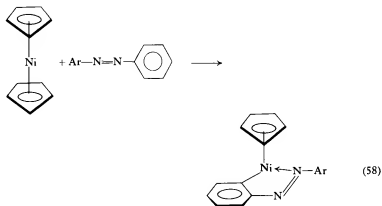
Table V summarizes C_5H_5 substitution with nickelocene.

Exchange of cyclopentadienyl ligands by their substituted analogs has been reported by Nesmeyanov, Ustynyuk, and Rodionova. They have studied the reaction of nickelocene with lithium α -phenyl(dimethylamino-methyl)cyclopentadienide (225).

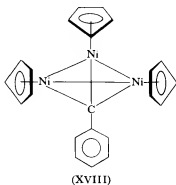


The reaction is smooth in ether-benzene solvent with a tenfold excess of the organolithium compound. In this reaction complete decomposition of nickelocene and formation of Ni^{2+} is not excluded; further reaction in the ordinary manner of metallocene synthesis to give the final reaction product could then occur.

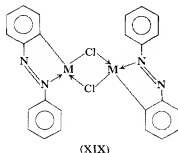
Of great interest is the reaction of nickelocene with azobenzene, first described by Kleiman and Dubeck (230),



Besides substitution of the $\pi\text{-C}_5\text{H}_5$ ligand by azobenzene there also occurs substitution of the ortho (with respect to the azo group) hydrogen. This is not the only example of a ring-hydrogen substitution during ligand exchange with nickelocene. For example, $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$ give (XVIII), based on NMR and mass spectra (231).



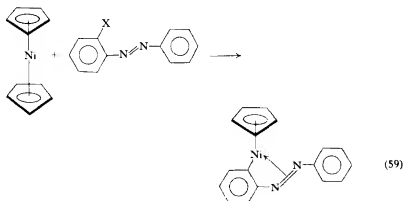
o-Hydrogen substitution has also been observed in reactions of azobenzene with PdCl_2 or K_2PtCl_4 , giving dimers (XIX) (232).



(XIX)

M = Pd, Pt

It has been shown that such substitution of hydrogen is probably electrophilic in nature since complex formation is more favorable with ortho- and para-directing substituents on the azobenzene nucleus. Ustynyuk and Barinov (233, 234) have studied the effects of substitution in azobenzene on the reaction with nickelocene, and thereby confirmed the electrophilic nature of the substitution. *o*-Halogen atoms may undergo substitution as well.



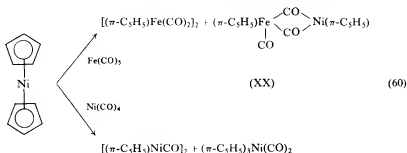
(59)

The reaction rate increases in the following order:



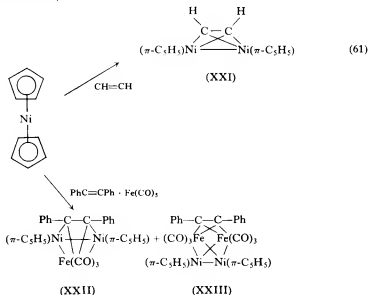
¹² Azobenzene transfer from one metal to another is described by Heck (235).

There is also information on the formation of bridged complexes on substitution of one ring in nickelocene. Thus nickel and iron carbonyls produce the following compounds on reacting in benzene (236–240):



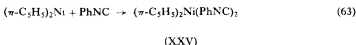
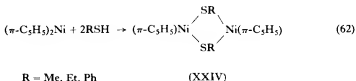
It is interesting that in essence complex (XX) is the result of cyclopentadienyl transfer from nickel to the iron atom. In Maitlis's opinion (180) the reaction mechanism resembles the tetraphenylcyclobutadiene transfer from palladium to the iron atom. In terms of CO substitution in the Fe and Ni carbonyls these are nucleophilic reactions in which nickelocene plays the role of a nucleophile.

Reaction of nickelocene with acetylenes affords complexes with Ni—Ni bonds (236–239, 241).

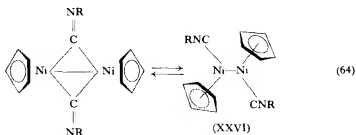


The synthesis and structure of similar complexes with perfluoro-substituted acetylenes has also been studied (242).

Reactions with thiols (243, 244) and isonitriles (245, 246) give binuclear compounds.



For isonitrile complexes the equilibrium shown takes place in solution (245). It is shifted in favor of the bridged form.



The solid complex has the structure (XXVI) (247). Moreover, complex (XXV) has been obtained from $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}$ and $\text{Ni}(\text{CNPh})_4$ in benzene (245).

Based on the results discussed, it may be concluded that ligand replacement in nickelocene follows an associative mechanism, and the electron density shift in the transition state is not decisive in the cyclopentadienyl exchange reaction.

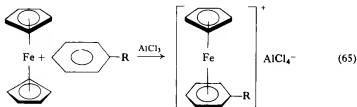
In ferrocene there are no sufficiently low vacant orbitals which could stimulate nucleophilic attack. Thus the cyclopentadienyl ligands do not undergo a nucleophilic A-type substitution. Moreover, in contrast to

nickelocene, with ferrocene only electrophilic reagents lead to substitution and exchange of the ligands, and only then under drastic conditions.

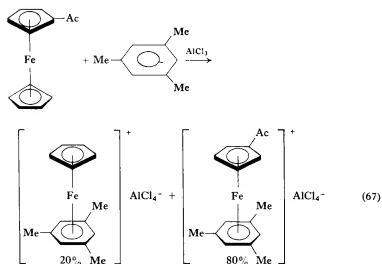
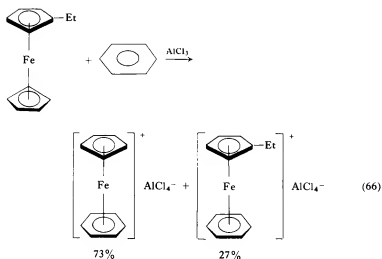
It has been found that ferrocene forms green complexes (probably via charge transfer) with aluminum chloride (248). Indeed, ferricenium salts $[\text{C}_{10}\text{H}_{10}\text{FeH}]^+[\text{AlCl}_4]^-$ form in protic media; their physical and chemical properties have been studied in detail by Pavlik *et al.* (249). In particular, it has been shown that the five-membered rings in this compound have a dihedral angle of about 140° . It may be assumed, therefore, that ferrocene and AlCl_3 also produce a charge-transfer complex with a similar distortion of geometry, and an increase in the metal's coordination number. As a result of charge transfer from the iron to aluminum chloride, the metal-cyclopentadienyl bond becomes weaker because of the decreasing metal ability to engage in retrodative bond formation. In the extreme case the metal-ring bond may be partly of the σ -type. Thus the molecule becomes coordinatively unsaturated, favoring subsequent ligand substitution in accord with the usual mechanism (see earlier).

It has been shown that heating ferrocene with AlCl_3 in inert media causes partial decomposition and the cleaved cyclopentadienyl groups enter as substituents in unreacted ferrocene molecules (250–253). In the presence of AlCl_3 , monoalkylferrocenes disproportionate to heteroannular disubstituted ferrocenes, the reaction being assumed to involve cleavage of the metal-ring bond (254).

Nesmeyanov, Volkenau *et al.* were the first to replace cyclopentadienyl with another ligand in ferrocene, preparing cyclopentadienyl-arene iron complexes by reaction of ferrocene with aromatic compounds in the presence of AlCl_3 (255–259).



Detailed investigation of the effect of substituents revealed that the cyclopentadienyl ring in which electron density is the highest always undergoes replacement predominantly (260).



Arenes with electron-attractive substituents do not react with ferrocene (260).

It can be assumed that AlCl_3 combines with the ring of highest electron density, rather than with the iron atom of ferrocene. This decreases the stability of the metal-ring bond, and stimulates further substitution in this ring. There are some data indicating that in charge-transfer complexes in

the solid an acceptor molecule occupies a place above the center of the five-membered aromatic ring (261).

Experimental data available at present are insufficient to permit establishment of the reaction mechanism for ring substitution in ferrocene and its analogs.

V

CONCLUSION

The majority of the reactions discussed in this review are initiated by coordination of the metal atom to an attacking substrate. In the intermediate thereby generated some change occurs in the character of the metal-leaving ligand bond, and as a result bond cleavage takes place. This mechanism corresponds to that of associative ligand substitution in inorganic transition metal complexes. For almost all the π -bonded polydentate-ligand transfer reactions discussed herein, a decrease of the coordinative ability of the ligand in a transition state is a common step. At a certain point in the reaction (which cannot always be established by experiment) the transferring ligand acts as a bridge between two metal atoms owing to a release of multiple bonds out of the original. Thus the transferring ligand is not a kinetically independent particle and predominantly retains its starting configuration. It is because of the latter fact that a stereospecificity of ligand transfer reactions arises which, as we have noted at the beginning, are models for elementary steps in homogeneous catalysis in the presence of transition metal π -complexes.

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Author Index

Numbers in parentheses are reference numbers and indicate that an author's work is referred to, although his name is not cited in the text. Numbers in italics show the page on which the complete reference is listed.

A

- Abeck, W., 170(261), *192*
- Abel, E. W., 116(1, 2), *186*, 199(5), 200
(1), 201(2), 210(1, 6), 215(4), 221
(2), 223(2), 224(2), 225(2), 226
(2), 233, 359(59), *411*
- Abele, G., 245(74), *269*, *271*
- Abeles, T. P., *190*
- Abramova, A. N., 9(48), 13(63), 34
(191), 37(246), *61*, *62*, *67*, *69*
- Adams, D. A., *233*
- Addison, C. C., 166(7), 182(5, 6, 7), *184*
(8), *186*
- Ahmad, M., 120(112), 121(13, 112), *174*
(112), *186*, *189*
- Ahmed Khalil, 32(171), *66*
- Alben, J. O., 164(41), *186*
- Alberola, A., 369(125), *412*
- Alekseev, N. V., 384(214), *415*
- Alferov, A. V., 374(155), *413*
- Alfonso, L., 21(104), *64*
- Allen, A. D., 116(15), *186*, 215(8), *233*,
350(20, 21), 353, 354(20, 21), *410*
- Alper, H., 161(16), *186*
- Amma, E. L., 366(97), *412*
- Anderson, J. S., 171(17), *186*, 356, *411*
- Anderson, M. M., 361(83), *411*
- Andrianov, V. G., 50(432), *77*
- Ang, H. G., 154(18), *186*
- Angelici, R. J., 116(21), 123(20, 23, 24),
124(108, 321), 170(19, 22, 24), 173
(19, 24, 108, 321), 174(24, 321),
178(22, 321), *186*, *188*, *194*, 215(9),
233, 362, 363(89), 381(186), *411*,
414
- Anisimov, K. N., 35(209, 210, 211), 36
(213, 214, 215, 216, 217, 218, 219,
220, 221, 222, 224, 225, 226), 37
(227, 228, 229, 230, 231, 232, 233
234, 235, 236, 237, 239, 240, 241,
242, 243, 244), 47(360, 361, 362,
363), 48(364, 365, 366, 367, 368,
369, 373, 374, 375, 376, 377), 49
(377, 379, 382, 383, 384), 56(451,
452, 453, 454, 455), 68, 69, 74, 75,
78, 124(372), 139(318), *195*, 223
(107, 108), 225(108), 226(107),
227(107), 230(108), 232(108), *235*
- Antonova, A. B., 36(218, 219, 224), 37
(227, 236, 240), *68*, *69*
- Anzenhofer, K., 357(46), *410*
- Apple, E. F., 243(107, 108), 264(2), *269*,
272
- Argento, B. J., 173(25), *186*
- Arimoto, F. S., 98(1), *111*
- Ariyaratne, J. K. P., 151(26), 159(26),
186
- Armstrong, A. T., 392(220), *415*
- Arndt, F., 17, *63*
- Arnett, E. M., 108, *111*
- Ashford, T. A., 357(45), *410*
- Ashley-Smith, J., 136(27), *187*, 357(40),
410
- Astakhova, I. S., 13(67), 54(438), *62*, *77*
- Atoji, M., 239(4), 240(4), 248(5), 250
(3), 252(4), *269*
- Augl, J. M., 143(443), 144(443, 444),
148(442), 171(444), *197*
- Aumann, R., 148(198, 199), 163(197,
198, 199), 166(197, 198, 199, 281),
186, *191*
- Auten, R. W., 240(6), 241(6), *269*
- Avoyan, R. A., 53(430), 77, 371(132),
412

B

- Babakhina, G. M., 53(435, 437, 439),
77, 373(147), *413*
- Babitskii, B. D., 371(129), *412*

- Babushkina, T. A., 51(415), 76
 Baddley, W. H., 116(29), 144(29), 146
 (31), 159(410a), 165(32), 176(30),
 178(30), 186, 187, 196, 355, 356,
 410
 Bader, G., 170(268), 172(268), 193
 Baenziger, N. C., 355(34), 410
 Bagga, M. M., 120(33), 126(33), 127
 (33), 132(34, 36), 136(36), 137
 (34), 157(35, 36), 187
 Baikie, P. E., 120(33, 38, 39, 40), 126
 (33), 127(33, 40), 137(39), 157
 (38), 165(37), 187
 Bailey, S. M., 248(106), 272
 Balch, A. L., 161(41), 182
 Banus, M. D., 239(94), 272
 Barinov, I. V., 404, 415
 Barnett, K. W., 149(446), 177(446), 197
 Barr, J. B., 250(7), 270
 Barraclough, C. C., 211(10), 212(10),
 233
 Barrett, J. H., 140(399), 196
 Barrett, P. F., 215(8), 233
 Barrill, R. W., 365(94), 412
 Barrow, M. J., 120(42), 137(42), 153
 (42), 187
 Bartell, L. S., 384(216), 388(216), 415
 Bartenstein, C., 170(267), 172(267), 193
 Baryshnikov, L. I., 47(363, 364), 49, 74,
 75
 Basolo, F., 116(43), 187, 348(1), 363
 (88), 367, 381(187, 188), 382(189),
 390(188), 409, 414
 Bass, C. D., 263(64), 271
 Bau, R., 201(26), 217(26), 219(26), 221
 (26), 233
 Bauder, M., 174(46), 185(46), 186(47),
 187
 Bauer, K., 132(44), 187
 Bauer, R. A., 139(45), 187
 Baukov, Yu. I., 21(112, 113, 114), 64
 Bayer, R., 124(181, 182), 190
 Bazhenova, A. V., 30(154), 66
 Beachell, H., 103, 104(11), 112
 Beachell, J. C., 104(3), 111
 Becconsall, J. K., 372(143), 413
 Becher, H. J., 248(8), 270
 Beck, W., 118(49), 173(50, 52, 338a,
 463a), 174(46, 48, 53), 176(51),
 185(46, 338a, 463a), 186(47),
 187, 194, 198, 201(12, 13), 211(11),
 212(11), 215(18), 217(12, 13), 221
 (13), 222(12, 13, 14), 224(14), 225
 (12, 14), 233
 Beckert, O., 397(278), 416
 Behrens, H., 168(54, 329), 169(55, 57,
 61), 170(53, 54, 55, 56, 57, 58, 58a,
 59, 60, 62, 63, 64, 65, 67, 329),
 171(183), 173(61, 83), 178(54, 55,
 66), 179(54, 55, 66), 185(59), 187,
 191, 194, 369(118), 399(281), 412,
 416
 Beinoravichute, Z. A., 38(254, 255, 256),
 70
 Belavin, I. Yu., 21(112, 113, 114), 64
 Beletskaya, I. P., 4(16), 60
 Bellama, J. M., 253(88), 257(88), 259
 (87), 271
 Belluco, U., 170(109), 173(109), 174
 (109), 188, 358(50), 363(87), 366
 (101), 411, 412
 Belozerskii, N. A., 382(190), 414
 Bel'skii, N. K., 32(167), 66
 Benedict, J. J., 151(447), 197
 Benkeser, R., 81(4), 102, 111
 Benlian, D., 217(16, 19), 223(16, 19),
 224(16, 19), 225(16), 227(16), 228
 (19), 229(16), 233
 Bennett, C., 263(89), 271
 Bennett, M. A., 144(68), 187, 352, 355,
 358(54), 359(59), 410, 411
 Bennett, R. P., 134(69), 182
 Benson, R. E., 98(5), 111, 161(344), 194
 Benzoni, L., 169(70), 171(70), 187
 Berlin, A. M., 50(407, 408), 51(407,
 408), 76, 384(201, 202), 414
 Berngruber, W., 144(200), 191
 Berry, R. A., 108, 109(40), 112
 Beschastnov, A. S., 36(215), 68
 Beutner, W., 119(262, 263, 264, 265),
 121(263, 265), 184(265), 193
 Biallas, M. J., 240(10), 269(9, 10, 95),
 270, 272
 Bigorgne, M., 199(17), 200, 211(120),
 217(16, 19, 114, 132), 221(85, 123),
 223(16, 19), 224(16, 19), 225(16),
 227(16), 228(19), 229(16), 233,
 235, 236, 358(58), 359(58), 411

- Billig, E., 211(64), 234
 Binder, W., 172(319), 194
 Birchall, T., 120(118), 164(118), 189
 Birmingham, J. M., 383(196), 414
 Bisnette, M. B., 56(448), 78, 124(310), 125(307, 308), 126(308), 176(309), 193, 194
 Blake, D. M., 176(71), 178(71), 187
 Bland, W. J., 142(72), 188
 Blaschette, A., 170(73), 188
 Blinova, V. A., 42(321), 43(321), 73
 Bly, R. S., 108(6, 7), 112
 Bochkarev, V. N., 51(418), 77
 Bocharov, D. V., 52, 77
 Bock, H., 131(80), 151(74, 75), 152(75, 76), 155(77, 79, 168), 164(76, 78), 186(47), 187, 188, 190
 Bock, R., 356, 410
 Böhme, H., 171(364), 172(364), 195
 Bogdanovic, B., 371(135, 136), 372(135), 374(153), 412, 413
 Bokova, A. P., 17(85), 63
 Bolesova, I. N., 44, 45(342, 344, 345, 348, 350, 353), 46(355), 73, 74, 86(50), 87(50), 91(53), 92(55), 113, 399 (255, 256, 257, 258, 259), 407(255, 256, 257, 258, 259), 416
 Bolton, E. S., 173(81), 188
 Bonati, F., 151(453, 454), 160(82, 83), 188, 197
 Bondarev, V. B., 38(257), 70
 Boone, J. L., 250(16), 270
 Booth, G., 178(86), 188
 Bor, G., 200(20), 201(20), 211(21), 212(21), 213(20), 214(20), 215(20), 217(20), 219(20), 233
 Borisov, A. E., 9(47, 48), 10(50), 12, 13 (63, 64, 66, 67, 68), 14, 25(126, 127, 128, 130, 131, 132, 133), 26 (135, 136), 30(136), 34(183, 184, 185, 186, 187, 188, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205), 37 (246), 61, 62, 64, 65, 67, 68, 69
 Borisovi, A. I., 34(192), 67
 Borod'ko, Yu. G., 116(87), 188
 Boss, B. L., 373(149), 413
 Boss, C. R., 52(429), 77
 Both, B. L., 140(84, 85), 151(84, 85), 188
 Bottomley, F., 116(15, 88), 186, 188
 Bower, L. M., 200(22, 24), 215(23), 233
 Braatz, J. A., 357(42), 410
 Brabetz, H., 149(258, 259), 192
 Bradford, C. W., 178(89), 188, 215(25), 233
 Brainina, E. M., 49(390), 50(399, 400, 404, 405), 52(420, 421, 422, 423), 75, 76, 77, 394(264, 265, 266, 267), 395(267, 268, 269), 416
 Brandt, A., 237(96), 239(96), 272
 Braterman, P. S., 201(26), 217(26), 219 (26), 221, 233
 Bratsev, V. A., 17(83), 21(83), 63
 Brault, A. T., 382(189), 414
 Brause, A. R., 359(49), 361(75a, 75b), 410, 411
 Braye, E. H., 157(90), 188
 Bregadze, V. I., 21(109), 64
 Breitschaft, S., 368(106), 412
 Bremer, M., 163(91), 182
 Bremer, N. J., 142(189), 143(189), 144 (189), 169(190), 170(190), 180 (190), 182(190), 191
 Bressan, M., 171(92), 188
 Bright, D., 161(93), 188
 Brinckman, F. E., 239(12), 264(11), 270
 Brintzinger, H., 117(94), 188, 384(216), 415
 Brotherton, R. J., 237(13), 239(13), 240 (14, 17), 241(13), 242(13), 243 (14, 15), 244(14, 18), 246(14), 249(17, 18), 250(13, 16), 251(13, 14), 270
 Brown, D. A., 140(95), 188, 211(27, 28), 217(27), 222, 225(27), 233, 369 (116), 379, 412, 413
 Brown, D. B., 170(96), 188
 Brown, E. L., 170(96), 188
 Brown, H. C., 256(19), 270
 Brown, M. P., 240(20), 270
 Brown, T. L., 199, 201(30, 53), 210(30), 217(53), 219(53), 220, 221(29, 53), 222(30, 53), 223(30, 53), 224(30), 225(30, 53), 229(53), 233, 234
 Brubaker, G. L., 240(21), 270
 Bruce, M. I., 133(97, 98), 137(98), 140 (99, 100), 157(99, 100), 188, 359 (60), 411

Bruce, R., 121(13), 186
 Brune, H. A., 400(288), 417
 Brunner, H., 169(101), 170(101, 101a), 188
 Bryukhova, E. V., 21(109), 57(415), 64, 76
 Bublitz, D. E., 93(8), 94(9), 98(38), 99(38), 100(38), 112, 407(254), 416
 Budzikiewicz, H., 95(10), 112
 Bulkin, B. J., 124(181, 182), 125(102, 180), 185, 190
 Bunbury, D. St. P., 153(202, 220), 191
 Bundel', Yu. G., 4(15, 16), 60
 Burg, A. B., 171(103), 188, 242(22), 270
 Burlachenko, G. S., 21(112), 64
 Burmeister, J. L., 168(104), 175(104, 105), 180(104, 107), 182(106), 188
 Burnelle, L., 210(31), 211(31), 233
 Busetto, L., 124(108), 170(22, 109), 173(108, 109), 174(109, 109a), 178(22), 185(109a), 186, 188
 Busby, H. T., Jr., 105, 112
 Bush, M. A., 120(112), 121(111, 112), 174(110, 112), 175(110, 111), 188, 189
 Bushick, R. D., 108, 111
 Buss, A., 143(443), 144(443, 444), 171(444), 197
 Butler, I. S., 201(2), 215(2), 221(2), 223(2), 224(2), 225(2), 226(2), 233
 Butter, S. A., 103, 104(3, 11), 111, 112
 Buttery, H. J., 215(32, 33, 34, 35), 217(32), 233, 234

C

Cais, M., 95(14), 108(13), 112, 365(96), 412
 Calderazzo, F., 109(33), 112, 110(114), 121(185), 122(113), 160(114a, 185a), 189, 191, 215(96), 235, 369(125), 412
 Camia, M., 169(70), 171(70), 187
 Campbell, C. D., 135(115), 137(115), 189
 Campbell, G. W., 242(22), 270

Candlin, J. P., 116(117), 184(116), 189
 Capen, G., 106(45), 113
 Carotti, A. A., 242(116), 272
 Carroll, D. G., 392(220), 415
 Carty, A. J., 120(118), 164(118), 189
 Cashman, D., 125(119), 189
 Cassal, J. M., 140(430), 197
 Cataliotti, R., 138(120), 189, 211(64), 234
 Caughey, W. S., 164(14), 186
 Ceron, P., 252(23), 253(23), 254(23), 257(23), 260(23), 266(23), 270
 Cetini, G., 354(23, 25), 355(23), 410
 Chabardes, P., 145(121), 189
 Chadwick, B. M., 168(122), 189
 Chambers, C., 253(24), 270
 Chapovskii, Yu. A., 55(444, 445, 446, 447), 56(449, 450), 77, 78, 125(373), 169(166), 170(166), 190, 195
 Charkoudian, J. C., 190
 Chatt, J., 116(125), 165(32), 178(86, 124), 187, 188, 189, 352, 353(15), 355(28, 29), 361(76), 362, 410, 411
 Chaudhari, F. M., 151(123), 189
 Chenskaya, T. B., 54(439), 77
 Chernenko, G. M., 374(155), 413
 Chiesa, A., 367, 412
 Chipman, D. M., 123(126), 189
 Chiswell, B., 169(127), 170(127), 189
 Christiansen, V. H., 175(105), 188
 Chu, T. L., 242(25), 270
 Chukovskaya, E. Ts., 35(212), 68
 Chumaevskii, N. A., 34(193), 67
 Churanov, S. S., 38(248), 70
 Churchill, M. R., 371(133), 412
 Claeys, E. G., 141(165), 148(165), 190
 Clark, H. C., 215(36), 234
 Clark, R. F., 399(282), 416
 Clark, R. J., 365(95), 412
 Clark, R. J. H., 178(89), 188, 211(37), 215(25, 38), 233, 234
 Clarke, R. E., 143(128, 218), 189, 191
 Cleare, M. J., 116(129), 189
 Clement, W. H., 357(43), 410
 Coates, G. E., 379(169), 413
 Coerver, H. J., 143(130), 189

- Coffey, C. E., 170(131), 171(131), 172(131), 173(131), 189
- Coleman, K. J., 138(132), 189
- Collins, R. L., 409(261), 416
- Collman, J. P., 129(133, 134, 137, 138), 135(135), 173(136, 138), 174(136), 175(134, 137, 138), 176(137, 138), 189
- Colton, R., 178(139), 189
- Commereuc, D., 119(139a), 189
- Connelly, N. G., 149(140), 189
- Connor, J. A., 165(144), 166(141, 142, 360), 167(143), 189, 195
- Cook, C. D., 190, 353(20, 21), 354(20, 21, 22), 357(41), 410
- Cook, D. J., 358(47), 410
- Cooke, J., 127(150, 151), 140(152, 153), 190
- Cooke, M., 359(60), 411
- Cookson, R. C., 379(173), 414
- Cope, A. C., 404(232), 415
- Coppens, P., 384(200), 414
- Corain, B., 171(42), 188
- Corey, E. J., 24, 64
- Cossee, P., 377(163), 378, 413
- Costello, W., 119(158), 120(158), 121(158), 190
- Cottis, S. G., 407(252, 253), 416
- Cotton, F. A., 116(146), 142(145), 143(145), 148(145), 162(148a), 153(402), 162(148a), 170(147, 239, 402), 172(147, 239), 175(147a), 178(148), 189, 190, 192, 196, 199(42), 200(40, 42, 43, 44, 45), 201(42), 213(39, 41, 95), 214(39), 234, 235, 383(193, 196), 394(263), 414, 416
- Coucovanis, D., 116(154), 190
- Coulson, C. A., 203(46), 210, 211(31), 233, 234
- Coulson, D. R., 351(10), 410
- Coutts, R. S. P., 129(155), 190
- Coyle, T. D., 249(85), 252(28), 253(29, 88), 254(27, 28), 255(27), 256(27), 257(27), 259(87), 261(28, 56), 262(28), 264(11), 268(28), 270, 271
- Craig, Taylor, R., 215(130), 236
- Craik, A. R. M., 134(157), 190
- Cramer, R., 360, 361(78, 81), 362(85), 391, 411
- Criegee, R., 400(287, 288), 417
- Cripps, H. N., 397(237), 416
- Croatto, U., 358(50), 411
- Crociani, B., 211(37), 234
- Crocker, D. C., 201(136), 217(136), 220, 221(136), 223(136), 230(163), 236
- Cross, P. C., 201(135), 202(135), 203(135), 213(135), 218(135), 236
- Crosse, B. C., 215(38), 234
- Cullen, W. R., 127(150, 151), 190
- Cundy, C. S., 144(219), 191
- Cunningham, D., 369(116), 412
- Curran, A. C., 143(130), 189
- Cutcliffe, A. B., 163(91), 188

D

- Dahl, L. F., 119(158), 120(158), 121(158), 149(140), 189, 190
- Dailey, B. P., 83(83), 114
- Dalton, J., 199(50), 201(52), 214(48), 215(4, 47, 48, 49, 50, 51), 218(52), 223(52), 226(52), 227(52), 233, 234
- Danen, W., 106(115), 112
- Dann, A. E., 240(20), 270
- Danyluk, S., 354(22), 410
- Darensbourg, D. J., 201(30, 53), 210(30), 217(53), 219(53), 220, 221(53), 222(30, 53), 223(30, 53), 224(30), 225(30, 53), 229(53), 233, 234
- Dashunin, V. M., 13(69), 62
- Davies, C. S., 138(132), 189
- Davies, W. O., 168(159), 190
- Davis, G. R., 352(14), 410
- Davis, R., 182(5), 184(5), 186
- Dawans, F., 359(65), 411
- Day, J. P., 381(187), 414
- Dayton, J. C., 171(103), 188
- Deardorff, E. A., 175(105), 188
- Deberitz, J., 141(416a), 196
- de Boer, J., 357(46), 410
- De Cian, A., 156(160), 190
- Decius, J. C., 201(135), 202(135), 203(135), 213(135), 218(135), 236
- Deck, H. R., 146(161), 190

- Deckelmann, E., 141(162, 163, 464), 190, 198
 Deever, W. R., 249(30), 270
 Dehnicke, K., 185(324), 194
 De Innocentiis, M., 169(70), 171(70), 187
 Dekker, M., 121(164), 122(164), 129(164), 131(164), 155(164), 173(81), 188, 190
 Delbeke, F. T., 141(165), 148(165), 190
 Demsey, J. N., 355(34), 410
 Denisov, F. S., 36(221, 222), 68
 Denisovich, L. I., 44(333), 46(355), 55(442), 56(450), 73, 74, 77, 78, 169(166), 170(166), 183(244), 190, 192, 375(160), 413
 Denton, D. L., 123(23), 186
 Deryabin, V. V., 45(346), 46(346), 74
 Dessy, R. E., 169(167), 170(167), 171(167), 190
 De Stefano, N. J., 182(106), 188
 Dewar, M. J. S., 355, 410
 Dibeler, V. H., 248(31, 32), 270
 Diener, W., 239(33), 270
 Dietrich, H., 371(131), 412
 DiPietro, C., 153(247), 154(247), 192
 Djerassi, C., 95(10), 112
 Dobrzanski, H., 171(183), 173(183), 191
 Dobson, G. R., 141(427), 142(172), 143(427), 148(172, 173, 428), 190, 197, 215(73, 74, 126, 127, 128, 129), 234, 236, 350(6), 409
 Dobson, J. E., 265(34), 270
 Dodge, R. P., 379(170), 413
 Doedens, R. J., 120(174, 175, 176, 177, 178), 122(175), 130(174), 131(176), 134(178), 137(177), 190
 Dolgoplosk, B. A., 371(137), 374(155), 413
 Dombrovskii, Ya., 30(154), 66
 Douek, I. C., 119(139a), 189
 Douglas, W. M., 171(450), 177(450), 178(450), 179(450), 197
 Dows, D. A., 168(179), 190
 Drozd, V. N., 38(262), 41(291, 298, 300), 42(298, 300, 301, 302, 303, 304, 308, 311, 312, 313, 314, 316, 317, 318), 43(323), 44(335, 336), 70, 72, 73, 74
 Dubeck, M., 393(222, 223) 397(230), 403, 405(241), 415
 Dubovitskii, V. A., 17(86), 50(406, 409), 51(406, 409, 411, 412, 413, 414, 415, 416, 417, 418, 419), 63, 76, 77, 384(202, 205, 206, 207, 208, 209, 210), 386(208, 209), 387(209), 414
 Dudek, E., 397(276), 406(242), 415, 416
 Duncanson, L., 355(28, 29), 359(27), 410
 Dunitz, J. D., 379(171), 413
 Dvoryantseva, G. G., 37(227, 229, 236, 237), 41(290), 50(391, 392), 57(416), 69, 71, 75, 76, 84, 87(16), 103(16, 17), 112, 223(107, 108), 225(108), 226(107), 227(107), 230(108), 232(108), 235, 384(209), 386(209), 387(209), 414
 Dyatkina, M. E., 383(192), 384(199), 414
- E**
- Edgar, K., 215(54), 234
 Edgell, W. F., 124(181, 182), 125(180), 190
 Edward, J. T., 161(16), 186
 Edwards, D. A., 147(179a), 190
 Eeckhaut, Z., 141(165), 148(165), 190
 Efraty, A., 380(178, 180), 381(180), 390(180, 181), 405(180), 414
 Efraty, M. B., 124(310), 194
 Egger, H., 89(72), 113
 Eichler, S., 145(419), 146(419), 196
 Eisenthal, R., 106(42), 112, 113
 Eliashevich, M., 210(55, 56), 234
 Ellermann, J., 171(183), 173(183), 191
 El-Sayed, M. F. A., 142(172), 143(184), 148(172), 190, 191, 201, 214, 215(58), 217(57), 234
 Englemann, H., 173(52, 338a, 463a), 174(52), 185(338a, 463a), 187, 194, 198, 215(15), 233
 Engelmann, T. R., 83(76, 77, 78), 84(73, 77), 85(77), 87(77), 94(79), 113, 114
 Epifanskii, P. F., 5(21), 60
 Ercoli, R., 116(114), 189, 369(125), 412
 Ernst, C. R., 80(75), 81(75), 83(75, 76, 77), 84(74, 75), 85(74, 77), 87(77), 114

Eskin, I. T., 5(23), 37(245), 60, 69
 Evans, W. H., 248(106), 272

F

Faingor, B. A., 21(109, 111), 64
 Falk, H., 132(44), 187
 Fano, L., 248(65), 271
 Faraone, F., 366(101), 412
 Farmery, K., 161(187, 188), 162(188),
 163(186, 187, 188), 191
 Farona, H., 215(65), 234
 Farona, M. F., 142(189, 192), 143(189,
 192), 144(189, 192), 144(191), 147
 (192), 148(191), 149(192), 163
 (91), 169(170), 170(170), 177(193,
 194, 465), 178(193, 194, 465, 466),
 179(194), 182(190), 188, 191, 198
 Fayer, M. D., 139(195), 191
 Fedin, E. I., 13(67), 21(108), 26(135),
 49(386), 50(393), 51(413, 414), 52
 (426), 53(433), 62, 64, 65, 75, 76,
 77, 81(36), 112, 183(375), 195, 384
 (206, 207), 407(252), 414, 416
 Feeney, J., 257(35), 270
 Fedorov, L. A., 49(386), 50(393), 75,
 76
 Fehhammer, W. P., 174(46, 48), 185
 (46), 186(47), 187
 Feldt, K., 176(51), 187
 Feltham, R. D., 191
 Fenn, R. H., 177(226), 178(276, 277),
 179(226, 227), 192
 Filbey, A. H., 393(222), 415
 Filimonova, N. P., 35(209), 68
 Filippov, O. F., 44(340), 73
 Finch, A., 239(38), 248(36, 37), 250(38),
 252(23), 253(23), 254(23), 257
 (23), 260(23), 266(23), 270
 Fiore, M., 151(454), 197
 Fischer, E. O., 52, 77, 139(45, 201, 207,
 208, 208a), 140(210), 144(209, 201),
 145(205, 206), 148(198, 199, 209),
 150(205, 206), 153(202), 163(197,
 198, 199, 203, 209), 165(37, 204),
 166(28, 141, 142, 197, 198, 199, 203,
 209, 256, 353, 354, 355, 356), 170
 (211, 212, 213), 186, 187, 189, 191,
 192, 194, 195, 356, 365(93), 368

(106, 108, 109, 113), 369(117, 122),
 373(152), 383(195), 394(262), 396
 (271, 272, 273, 274), 397(240, 278),
 405(240), 411, 412, 413, 414, 415,
 416
 Fischer, H., 237(96), 239(96), 272
 Fischer, R. D., 199(60), 223(61), 227
 (61), 234
 Fish, R. W., 263(89), 271
 Fitton, P., 173(25), 186
 Flannigan, W. T., 121(214), 122(214),
 132(34), 137(34), 157(35, 405), 158
 (215), 175(214), 187, 191, 196
 Flegontov, A. I., 5(21), 60
 Fleischer, E. B., 163(216, 217), 164(216,
 217, 461), 191, 197
 Flid, R. M., 352, 353, 410
 Flitcroft, N., 215(62, 63), 234
 Floriani, C., 160(114a, 185a), 189, 191
 Flynn, T. P., 172(295), 193
 Foffani, A., 138(120), 189, 211(64), 234
 Ford, P. C., 143(128, 218), 189, 191
 Forg, F., 400(288), 417
 Forster, A., 144(219), 191
 Fox, V. L., 17(88), 63
 Fox, W. B., 239(110), 260, 263(39), 266
 (39), 270, 272
 Frank, E., 153(202, 220), 191
 Fraser, M. S., 146(31), 159(410a), 186,
 196, 356, 410
 Frazee, L. M., 169(190), 170(190), 180
 (190), 182(190), 191
 Frazer, J. W., 239(40), 270
 Freidlina, R. Kh., 9(43), 10(55), 11(55,
 57), 12, 13, 14, 22(115, 116), 23
 (116, 117), 34(181), 35(212), 50
 (395, 396, 397, 398, 399, 400, 402,
 403, 404, 405), 52(420, 421, 422,
 423), 61, 64, 68, 76, 77, 394(264,
 265, 266, 267), 395(267, 268, 269),
 396(269), 416
 Frey, J., 252(23), 253(23), 254(23), 257
 (23), 260(23), 266(23), 270
 Frey, V., 119(221), 121(221), 191
 Friedel, H., 148(170), 149(170, 171), 152
 (169), 190
 Friiz, H. P., 145(222), 191, 383(195),
 414

Fritz, P., 240(75, 76, 77), 241(77), 243(76), 244(76), 245(76) 246(77), 251(76), 271
 Fronzaglia, A., 124(310), 138(311), 144(312, 314), 148(312, 313, 314), 194
 Fukuoka, S., 124(223), 192

G

Gall, H., 171(333), 194
 Gallini, J. B., 172(295), 193
 Gambaryan, N. P., 52, 77
 Gambino, O., 354(23, 25), 355(23), 410
 Gamble, E. L., 239(94), 272
 Games, M. L., 379(175), 380(176, 177, 178, 182), 382(177), 390(182), 414
 Gandilhon, P., 145(121), 189
 Ganorkar, M. C., 368(112), 412
 Gardner, P. J., 248(36), 270
 Garner, A. W. B., 117(352), 195
 Gassenheimer, B., 247(41), 270
 Gatti, A. R., 253(118), 254(118), 255(118), 272
 Gauthier, G. J., 94(18), 112
 Gayles, J. N. 248(42), 270
 Gerasimenko, A. V., 42(303, 305), 43(322), 72, 73
 Gerlach, K., 148(437), 197
 Gernert, F., 383(197), 414
 Gerrard, W., 143(224), 192
 Gey, G., 359(271), 410
 Giddings, S. A., 357(44), 410
 Gilbert, J. D., 150(224a), 192
 Gill, G. B., 140(225), 192
 Ginsberg, A. P., 192
 Gipp, N. K., 4(10), 60
 Girard, C., 145(121), 189
 Girshovich, A. S., 50(408), 57(408), 76
 Glass, W. K., 369(116), 412
 Glicenstein, L. J., 253(91), 254(91), 255(91), 265(91), 271
 Glushnev, N. F., 5(21), 60
 Gogan, N. J., 138(132), 189
 Gol'danskii, V. I., 21(107, 110), 64
 Goldblatt, M., 200(83), 235
 Goldberg, S. I., 407(250), 416

Golenko, T. G., 374(155), 413
 Golovchenko, L. S., 21(108, 109), 64
 Golovnya, R. V., 37(247), 38(247, 260), 40(281), 69, 70, 71
 Gonsales, A., 30(153), 66
 Goodwin, H. A., 139(201), 144(201), 191
 Gordon, G., 239(12), 270
 Gosteva, G. N., 71
 Gourlay, N., 140(225), 192
 Gow, A., 361(80), 411
 Graham, A. J., 168(159), 177(226), 178(276, 279), 179(226, 227), 190, 192
 Graham, J. R., 363(89), 411
 Graham, W. A. G., 141(228), 192, 199(117), 215(76, 117, 118, 231), 218(117), 234, 235, 236
 Grandberg, K. I., 40(284), 41(284, 285), 44(331), 70, 71, 73, 84(16), 87(16), 90(19, 20), 103(16), 107(22), 108(51, 61), 109(51, 61), 112, 113
 Grasselli, J. G., 143(413), 144(413, 444), 146(191, 413), 148(191, 413), 171(444), 191, 196, 197, 215(124), 236
 Graziani, M., 363(87, 88), 411
 Gray, H. B., 215(65), 234, 348(3), 350(3), 409
 Graybill, B. M., 249(43), 270
 Greatrex, R., 118(229), 192
 Green, L. G., 248(45, 46), 271
 Green, M., 127(150, 151), 135(232), 136(27), 140(152, 153, 219, 233), 151(230), 153(231), 186, 190, 191, 192, 357(39), 358(47), 359(60, 64), 410, 411
 Green, M. L. H., 125(237), 126(236), 141(234), 151(26), 159(26), 182(235), 186, 192, 371(128), 379(169), 412, 413
 Greenwood, N. N., 118(229), 192
 Grib, A. V., 7(37), 61
 Gribov, L. A., 199, 231(65a), 234
 Griffith, W. P., 116(238), 171(239, 240), 172(239), 192
 Grimme, W., 242(44), 271

Grinberg, A. A., 178(241), 183(241), 192
 Grundy, K. R., 154(243), 184(242), 192
 Gscheidmeier, M., 119(266), 193
 Gubenko, N. T., 32(172, 173, 174, 175), 66
 Gubin, S. P., 37(238), 39(273), 40(282, 284, 285, 286, 287, 288, 289), 41 (284, 285), 46(355), 54(441, 442, 443), 69, 71, 74, 77, 84(16), 87(16), 90(19, 20), 94(23), 98(21, 25), 99 (62), 103(16), 107(22), 108(23, 24, 51, 61), 109(32, 51, 61), 110(21), 112, 113, 169(166), 170(166), 183 (244), 190, 192, 371(134), 374 (158), 375(158, 160, 161), 376 (161), 377(158, 161), 378(161), 384(212, 213), 388(212), 389(212, 213), 392(221), 412, 413, 415
 Günther, H., 140(245), 192
 Gunn, S. R., 248(45, 46), 271
 Gustorf, E. K., *see* Koerner von Gus-
 torf, E.
 Gus'kova, A. N., 13(66), 25(126), 62, 64
 Gutmann, V., 350(71), 410
 Gутtenberger, J. F., 142(248, 431), 146 (250), 148(250), 169(249), 170 (249), 172(249), 173(248), 192, 197
 Guy, R. G., 352(16), 355(28, 29), 410

H

Haas, H., 143(471), 145(471), 148(471), 198
 Hafner, N., 397(278), 416
 Hafner, W., 394(262), 396(271), 416
 Hagen, A. P., 215(66, 67), 234
 Hagihara, N., 193, 359(62), 368(105), 396(275), 397(245, 280), 398(280), 404(245), 411, 412, 415, 416
 Hales, L. A. W., 211(69), 212(69), 215 (69), 234
 Haley, R. C., 81(60), 112
 Hall, D. W., 81(26), 98(28), 99, 102 (27), 107(26), 112
 Halow, I., 248(106), 272
 Haluska, R. J., 140(399), 196

Hanna, J. A., 159(440a), 160(440a), 197
 Harbourn, D. A., 215(62), 234
 Harder, N., 170(53), 187
 Hardt, P., 371(135), 372(134, 135), 412, 413
 Harechal, J. C., 359(65), 411
 Harris, C. B., 139(195), 191
 Hartley, F. R., 355, 410
 Hartmann, P., 144(433), 197
 Hashmi, M. A., 192
 Haszeldine, R. N., 140(84, 85), 151(84, 85), 188
 Hats, K., 104(70), 113
 Haven, A. C., 98(1), 141
 Hawkes, M. J., 192
 Hawthorne, M. F., 384(212a), 392 (212a), 415
 Hayter, R. G., 148(253), 192
 Heck, R. F., 52(429), 77, 118(255), 133 (254), 192, 373(149), 375, 378, 381 (185), 391(219), 404, 413, 414, 415
 Heckl, B., 166(256), 192
 Hedberg, K., 248(47), 271
 Heimbach, P., 371(135, 136), 372(135), 412, 413
 Hein, F., 369(119, 121, 123, 124), 412
 Heinemann, H., 361(80), 411
 Heintz, E. A., 170(257), 192
 Hellmann, H., 142(432), 149(432, 434, 438), 197
 Hendrick, D. G., 148(409a), 196
 Henry, M. C., 153(247), 154(247), 192
 Henry, P. M., 381(185), 414
 Henry, R. J. M., 170(147), 172(147), 189
 Henzi, R., 160(114a), 189
 Herberhold, M., 139(384a), 149(258, 259), 192, 195, 356, 411
 Hermannsdörfer, K. H., 241(48), 271
 Herrmann, D., 168(54), 169(55), 170 (54, 55, 56), 178(54, 55, 66), 179 (54, 55, 66), 187
 Hess, K., 15, 62
 Hess, R. W., 151(447), 197
 Hewertson, W., 352(14), 410
 Hewitt, T. G., 358(47), 410
 Hey, D. H., 6, 61
 Hidai, M., 143(351), 165(351), 195

Hieber, W., 119(221, 262, 263, 264, 265, 266), 121(221, 263, 264, 271, 272), 124(266a), 170(261, 267, 268, 270, 271), 172(267, 268), 184(265), 191, 192, 193

Hileman, J. C., 215(70), 234

Hill, E. A., 81(26), 107(26), 112

Hillier, I. H., 210(138), 236

Hilton, J., 178(273), 193

Hiraishi, J., 356(35a), 410

Hirshovich, A. S., 384(202), 414

Hoare, R. J., 134(157), 190

Hoehn, H. H., 397(237), 416

Hoh, G. L., 98(29, 38), 99(38), 100(29, 38), 112

Holliday, A. K., 237(56), 239(52, 70), 246(49), 250(50), 252(55, 56), 253(24), 257(35), 262, 264(51, 55, 57), 265(53, 54), 266(53), 270, 271

Holm, A., 175(282), 193

Holm, R. H., 161(41), 187

Holmes, J. D., 109(30), 112

Holzmann, R. T., 239(40), 270, 271

Hooz, J., 81(4), 102(4), 111

Horiie, S., 157(361), 195

Hornig, D. F., 203(71), 234

Horrocks, W. D., 211(72), 215(130), 234, 236, 381(183), 414

Hosking, J. W., 173(136), 174(136), 189

Houk, L. W., 215(73, 74), 234

Howells, W. G., 102(69), 113

Howk, B. W., 397(237), 416

Hübel, W., 157(90), 188

Hückel, W., 17, 63

Hüttel, R., 358(52), 411

Huge-Jensen, E., 175(282), 193

Huggins, D. K., 215(63, 70), 234

Hughes, F. J., 211(27), 217(27), 222, 225(27), 233

Hull, C. G., 121(274), 178(274), 193

Hunt, D. F., 364(90), 411

Hunt, D. W., 240(20), 270

Huttner, G., 165(275), 193

Hyams, I. J., 248(36, 37), 270

I

Ibers, J. A., 120(178), 134(178), 159(410a), 190, 196

Ingold, C. K., 348, 409

Interrante, L. V., 358(54), 411

Ioganson, A. A., 37(239, 240, 242, 243, 244), 69

Iqbal, M. Z., 133(97, 98), 137(98), 188

Irving, R. J., 211(69), 212(69), 215(68), 234

Irwin, F., 6, 7, 61

Irwin, W. J., 357(38), 410

Isaeva, L. S., 4(18), 7(33, 37, 38, 39), 8(40), 45(349, 350, 353), 46(354), 60, 74, 86(50), 87(50), 113

Ishii, Y., 373(151), 413

J

Jacobson, R. A., 123(126), 189

Jaffé, H. H., 360, 411

Jain, S. C., 144(276), 148(276), 193

James, T. A., 400(289, 290), 417

Janes, D. L., 350(8), 410

Jarchow, O., 193

Jarvis, J. A. J., 120(278), 122(278), 193

Jauhal, G. S., 190, 357(41), 410

Jellinek, F., 393(224), 398(224), 415

Jennings, M. A., 169(280, 281), 170(280, 281), 177(279), 178(279), 179(279), 180(280, 281), 181, 193

Jensen, A., 175(105), 188

Jensen, K. A., 175(282), 193

Jessop, G. N., 246(49), 250(50), 264(51), 271

Jetz, W., 215(76), 234

Jira, R., 396(273, 274), 416

Job, A., 171(283), 193

Job, B. E., 120(278), 122(278), 193, 372(143), 413

Joh, T., 193, 396(275), 416

Johnson, A. W., 140(225), 192

Johnson, B. F. G., 116(286), 193, 201(77), 217(21), 219(21), 221, 222(77), 224(77), 235

Johnson, E. C., 183(287), 193

Johnson, J. D., 99(43, 44), 100(43, 44), 113

Johnson, N. P., 168(159), 190

Johnson, P. M., 168(159), 190

Johnson, S. M., 140(399), 196

Jonassen, H. B., 352(17), 410

Jones, D. A. K., 109(30), 112
 Jones, D. W., 379(173, 175), 414
 Jones, E. M., 167(143), 189
 Jones, L. H., 200(78, 79, 83), 235
 Jones, R. N., 199, 204(125), 223(125),
 224(125), 231(125), 236
 Jones, W., 83(77), 85(77), 87(77), 114
 Jones, W. J., 200(84), 235
 Joos, K., 173(338a), 185(338a), 194
 Joshi, K. K., 138(288, 289), 184(116),
 189, 193, 406(247), 415
 Joy, J. R., 356(69, 70), 411
 Jukov, A. P., 21(111), 64
 Jula, T. F., 144(290), 193
 Jun, M. J. 153(246), 154(246), 192

K

Kabachnik, M. I., 14(72), 20(72, 96),
 62, 63
 Kämpfer, K., 168(291), 193
 Kaesz, H. D., 143(413), 144(413), 146
 (413), 148(413), 196, 201(26), 214,
 215(58, 63, 70, 124), 217(26), 219
 (26), 221(26), 233, 234, 236, 365
 (94), 412
 Kaganovich, V. S., 33(178, 179), 34
 (180), 67
 Kahlen, N., 124(266a), 193
 Kahn, E. I., 4(3), 5(22), 60
 Kahn, O., 221(85), 235
 Kakudo, M., 120(342, 343), 122(342,
 343), 194
 Kakurina, L. N., 70
 Kalyavina, R. M., 42(321), 43(321), 73
 Kang, J. W., 129(134, 138), 135(135), 156
 (292), 173(138), 175(134, 138), 176
 (138), 189, 193
 Kangas, L. R., 381(185), 414
 Kannan, P., 108, 109(40), 112
 Kaplan, F., 359(49), 410
 Kaplan, P. D., 351, 361(75a), 410, 411
 Kartle, K., 369(123, 124), 412
 Kasai, N., 120(342, 343), 122(342, 343),
 194
 Kasperl, H., 171(365), 172(365), 195
 Kawai, K., 203(86, 105, 106), 235
 Kazankova, M. A., 17(87), 21(87), 63
 Kazitsyna, L. A., 17(82), 30(162), 63,
 66, 104(31), 105(31), 112
 Keable, H. R., 161(293, 294), 162(293),
 163(293, 294), 193
 Keeling, G., 215(32, 33, 34, 35), 217(32),
 219(87), 221(87), 222(87), 233,
 234, 235
 Keim, W., 371(135), 372(135), 374(154),
 412, 413
 Keleksaeva, T. G., 29(147, 148), 31(147,
 148), 65
 Kemmitt, R. D. W., 142(72), 188
 Kennedy, J., 351(11), 410
 Kenny, D. J., 172(295), 193
 Keppie, S. H., 141(296), 144(296), 193
 Kerrigan, J., 252(23, 102), 253(23), 254
 (23), 257(23), 260(23), 266(23,
 102), 267(102), 270, 272
 Ketley, A. D., 357(42), 410
 Kettle, S. F. A., 143(297), 144(297), 193,
 209(88, 89, 90, 93), 215(32, 33, 34,
 35, 91), 217(32, 92), 218(91), 219
 (87), 221(87), 222(87), 233, 234,
 235
 Khandkarova, V. S., 94(23), 108(23),
 109, 112
 Khandozhko, V. N., 36(214, 220, 223,
 225, 226), 68, 69
 Kharasch, M. S., 357(45), 410
 Khatami, A. I., 81(36), 112
 Khomutov, E. D., 66
 Khomutov, R. M., 16(80), 17(80, 84, 86,
 89), 63
 Khorlina, M. L., 5(26a), 61
 Khrapov, V. V., 21(107, 110), 64
 Kilbourn, B. T., 120(278), 122(278), 193,
 374(157), 413
 Kiener, V., 153(202), 191
 Kilner, M., 157(298), 161(187, 188, 293,
 294, 299, 300, 301), 162(188, 293,
 299, 300, 301), 163(186, 187, 188,
 293, 294, 300, 301), 182(6, 7), 184
 (8), 186, 191, 193
 King, R. B., 56(448), 78, 119(158), 120
 (158), 121(158), 123(303), 124
 (310), 125(307, 308), 126(308), 138
 (311), 144(305, 312, 314), 148(305,
 312, 313, 314), 150(315), 169(167,

- King, R. B. (*cont.*)
 304), 170(167, 304), 172(304), 173
 (304), 176(309), 190, 193, 194, 359
 (61), 391(218), 411, 415
- Kisin, N. V., 55(446), 78
- Kislyakova, N. V., 39(277), 40(280), 49
 (382, 383, 384), 71, 75, 81(49), 113
- Klabunde, U., 194
- Kleiman, J. P., 397(230), 403, 415
- Kleinberg, J., 98(29), 100(29), 109(46),
 112, 113
- Kleinwächter, F., 319(120), 412
- Klimova, V. A., 4(7), 60
- Klopman, G., 109(33), 112, 223(94), 227
 (94), 230(94), 235
- Knauss, L., 163(203), 166(203), 191
- Knipple, W. R., 148(442), 197
- Knol', P. G., 4(12), 25(129), 60, 65
- Knoll, F. J., 144(444), 171(444), 197
- Knox, G. R., 81(34, 60), 82(34), 112,
 113, 120(112), 121(13, 112, 164,
 214), 122(164, 214), 129(164), 131
 (164), 132(34), 134(157), 137(34),
 151(123), 155(164), 157(35, 405),
 158(215), 173(81, 317), 174(112,
 317), 175(214), 186, 187, 188, 189,
 190, 191, 194, 196
- Knox, J. R., 126(318), 194
- Kobayashi-Tamura, H., 159(384b), 195
- Kochergin, P. M., 21(106), 64
- Kocheshkov, K. A., 4(7, 8, 9, 17), 9(49),
 10(51, 54, 55), 11(55), 13, 22(115,
 116), 23(146), 35, 60, 61, 62, 64, 68
- Kochetkov, N. K., 29(146), 30(153, 156,
 158, 159, 161, 162, 163), 31(146, 156,
 165, 166), 34(181), 65, 66, 67
- Kochetkova, N. S., 38(248, 249, 250, 251,
 257), 39(263), 40(280), 49(381,
 385, 388, 389, 390, 391), 50(393,
 394), 51(414), 70, 71, 75, 76, 81
 (49), 113, 384(207), 407(251), 414,
 416
- Koerner von Gustorf, E., 153(246, 247),
 154(246, 247), 192
- Köster, R., 242(44), 271
- Koga, M., 104(70), 113
- Kohler, J., 169(57), 170(57, 58), 187
- Koizumi, N., 124(181, 182), 190
- Kollmeier, H. J., 165(204), 191
- Kolobova, N. E., 36(213, 214, 215, 216,
 217, 218, 219, 220, 221, 222, 223,
 224, 225, 226), 37(227, 228, 229,
 230, 231, 232, 233, 234, 235, 236,
 237, 238, 239, 240, 241, 242, 243,
 244), 47(360, 361, 362, 363, 364,
 366, 367, 368), 48(369, 377), 49(372,
 377, 379, 382, 383, 384), 56(451, 452,
 453, 454, 455), 68, 74, 75, 78, 124
 (372), 139(378), 195, 223(107,
 108), 225(108), 226(107), 227
 (107), 230(108), 232(108), 235,
 396(270), 416
- Kolomnikov, I. S., 36(213), 68
- Komenda, J., 98(35), 112
- Kompa, K. L., 131(80), 188
- Kormer, V. A., 371(129), 412
- Korneva, L. I., 31(164), 66
- Kotz, J. C., 263, 271
- Kovshov, E. I., 38(257), 70
- Kozlovskii, A. G., 37(238), 42(306), 69,
 72, 108(51), 109(51), 113
- Kraihanzel, C. S., 200, 213(41, 95), 234,
 235, 358(51), 411
- Krakkay, T. von, 171(366), 195
- Krasnoslobodskaya, L. L., 124(372), 195
- Kraus, C. A., 240(6), 241(6), 269
- Kraus, K. F., 142(192), 143(192), 191
- Kravtsov, D. N., 21(97, 98, 99, 100, 101,
 102, 103, 104, 105, 106, 107, 108,
 109, 110), 63, 64
- Kreiter, C. G., 139(45, 201), 144(200,
 201), 187, 191
- Kreys, Z. S., 17(85), 63
- Kritskaya, I. I., 23(120), 39(274, 275),
 44(332), 52(426), 53(430, 433, 434,
 435, 436, 437), 54(438, 439), 64,
 71, 73, 77, 183(374, 375, 376), 195,
 371(132), 373(147), 412, 413
- Kröner, M., 358(53), 371(135), 372
 (135), 411, 412
- Krogmann, K., 152(320), 172(319), 194
- Kruck, T., 368(110), 412
- Kruglova, N. V., 7(34), 61
- Kruse, A. E., 123(24), 124(321), 170
 (24), 173(24, 321), 174(29, 321),
 178(321), 186, 194

Kubota, M., 129(137, 138), 173(138),
175(137, 138), 176(71, 137, 138),
178(71), 187, 189
Kudriashov, L. I., 30(157), 66
Kudryavtsev, R. V., 53(436), 77, 183
(376), 195
Kuhn, S. J., 259, 271
Kuo, H. S., 242(63), 271
Kurland, R. J., 84(73), 113
Kursanov, D. N., 23, 24, 39(277, 278),
40(280), 49(382, 383, 384), 64, 71,
75, 81(36, 37, 48, 49), 112, 113, 393
(276), 415
Kuse, T., 143(351), 165(351), 195
Kuwana, T., 98, 99, 100(38), 112
Kuznetsova, N. I., 41(295, 296), 71, 72
Kvasov, B. A., 21(108), 51(419), 64, 77
109(32), 112

L

Laing, K. R., 178(322b), 183(322), 184
(242), 185(322b), 192, 194
Lalor, F. J., 125(119), 129(323), 189, 194
Landini, D., 27(142), 65
Lander, A., 351(11), 410
Landor, E. B., 17(92), 63
Landsfeld, H., 383(197, 198), 414
Lange, G., 185(324), 194
Lange, S., 165(275), 193
Langford, C. H., 348(3), 350(3), 409
Langhäuser, W., 148(439), 197
Lappert, M. F., 127(325), 131(325), 141
(296), 143(224), 144(296), 192,
193, 194
Lawson, D. N., 171(326), 172(326), 178
(327), 194
Lazareva, N. A., 50(406), 51(406, 411,
413, 416, 419), 76, 77, 384(202, 209,
211), 386(209), 387(209), 414, 415
Leach, R. E., 381(186), 414
Leden, I., 361(76), 411
Lehnert, G., 170(58a), 185(59), 187
Leites, L. A., 55(443), 77, 375(161), 376
(161), 377(161), 378(161), 413
Leonova, E. V., 49(386, 389), 75
Leont'eva, L. I., 44(338, 339, 340, 341),
71, 73

L'Eplattenier, F., 121(185), 160(114a,
185a), 189, 191, 215(96), 235
Leschcheva, I. F., 32(172, 173, 174), 66,
86(50), 87(50), 113
Levenberg, M. I., 83(39), 112
Levison, J. J., 183(328), 194
Lewis, J., 201(77), 211(10), 212(10), 215
(54, 97, 98), 217(77), 219(77), 221
(77), 222(77), 224(77), 233, 234,
235
Lewis, R., 84(73), 113
Liehr, A. D., 199(42), 200(42), 201(42),
234
Lillya, C. P., 364(90), 411
Lindenbergh, B., 173(338a), 185(338a),
194
Lindley, P. F., 153(202), 191
Lindner, E., 168(329), 169(61), 170(59,
60, 61, 64, 65, 329), 171(63), 173
(61), 174(61), 178(66), 179(66),
185(59), 187, 194
Lindsay, R. V., 98(5), 111
Lipscorn, W. N., 239(4), 240(4), 248
(5, 100), 250(3), 252(4), 269, 272
Lisichkina, I. N., 8(42), 61
Liston, S. K., 248(31), 270
Little, W. F., 99(43, 44), 100(43, 44),
106(42), 108, 109, 112, 113
Lloyd, J. P., 167(143), 189
Lobach, M. I., 371(129), 412
Loewen, W., 362, 411
Logar, N., 182(5), 184(5), 186
Lokshin, B. V., 21(104), 37(235, 239,
240), 51(417), 55(446), 56(450),
64, 67, 69, 76, 78, 104(31), 105(31),
112, 384(210, 211), 414, 415
Long, G. G., 89(72), 113
Languet-Higgins, H. C., 378, 413
Lovea, A. S., 5(26a), 61
Lottes, K., 211(11), 212(11), 233
Louterlier, A., 200(99), 235
Lubovich, A. A., 39(273), 71, 108(24),
112
Lucas, H. J., 355(35), 410
Ludwig, P., 400(287), 417
Luknar, N., 215(91), 218(91), 235
Lukyants, E. A., 399(286), 417
Lupin, M. S., 95(14), 112, 183(330), 194

Lutsenko, I. F., 5(24), 11, 15, 16(78, 80, 81), 17(80, 81, 82, 83, 84, 85, 86, 87, 88, 89), 21(112, 113, 114), 61, 62, 63, 64
 Luxmoore, A. R., 144(331), 194
 Lyakhovetsky, Yu. I., 53(436), 77, 183 (376), 195
 Lynch, J. A., 125(102), 188
 Lynds, L., 263(64), 271
 Lynn, K. N., 99(43), 100(43), 113

M

McAllister, C. G., 399(282), 416
 McBride, D. W., 397(276), 406(242), 415, 416
 McClellan, W. R., 161(344), 194, 397 (237), 416
 McCleverty, J. A., 116(286, 345), 193, 194, 400(289, 290), 417
 McCloskey, A. L., 240(14, 17), 243(14, 15), 244(14), 246(14), 249(17), 250 (16), 251(14), 270
 McClure, F. T., 6, 7, 61
 McCormack, C. G., 140(95), 188
 MacDiarmid, A. G., 215(66, 67), 234
 McDonnell, J., 106(45), 113
 McDowell, R. S., 200(83), 235
 McEwen, W. E., 98(29), 100(29), 109 (46), 112, 113
 McGlinchey, M. J., 131(346), 194
 McGlynn, S. P., 392(220), 415
 McKean, D. C., 203(71), 234
 McKeon, J. E., 173(25), 186
 MacNeven, W., 357(44), 410
 McPhail, A. T., 173(317), 174(317), 194
 McQuillin, F. H., 357(38), 410
 McWhinnie, W. R., 116(347), 194
 Madden, D. P., 120(118), 164(118), 189
 Magee, T. A., 368(111), 412
 Mahendran, M., 140(225), 192
 Maher, J. P., 171(332), 172(332), 194
 Maire, J., 85(82), 114
 Mais, R. H. B., 120(278), 122(278), 193, 352(14), 374(157), 410, 413
 Maitlis, P. M., 156(292), 193, 379(167, 172, 174, 175), 380(174, 176, 177,

178, 180, 182), 381(174, 181), 382 (177), 390(180, 181, 182), 405 (180), 413, 414
 Makarov, Yu. V., 48(372, 377), 49(377), 75
 Makarova, A. I., 39(264), 70
 Makarova, L. G., 4(5, 6, 8, 10, 32), 5 (19), 6(32), 7(30), 10(52), 55(444, 446, 447), 60, 61, 62, 77, 78, 125 (373), 195
 Maksimov, V. I., 23(118), 64
 Malatesta, L., 116(335), 194
 Malygina, I. A., 38(256), 70
 Manasevit, H. M., 240(14), 243(14), 244 (14), 246(14), 250(10), 251(44), 270
 Manchot, W., 10, 62, 170(334), 171(333), 172(334), 194
 Mann, D. E., 248(65), 271
 Mann, R. H., 211(72), 234
 Manning, A. R., 201(103), 215(54, 97, 98, 100, 101), 217(103), 219, 221 (103), 234, 235, 391(217), 415
 Manning, J. A., 109(46), 113
 Manuel, T. A., 115(337), 116(337), 121 (336, 338), 141, 175(336), 194, 358 (57), 359(57), 411
 Maoz, N., 365(96), 412
 Margerum, D. W., 350(8), 410
 Markina, V. Yu., 249(72), 271
 Marko, L., 123(395), 196
 Marsden, F. J., 257(35), 270
 Martins, C., 17(91), 63
 Mason, J. G., 99, 113
 Mason, R., 173(338a), 185(338a), 194, 371(133), 412
 Massey, A. G., 144(339), 146(339, 340), 148(409), 182(235), 192, 194, 196, 237(56, 67), 239(52, 70, 71), 250 (69), 252(55, 56, 68), 264(51, 66, 67), 265(53, 54), 266(53), 271
 Matejckova, E., 241(48), 271
 Materikova, R. B., 7(34), 15(76), 49(385, 386, 388, 389, 390, 391, 392), 50 (393), 61, 63, 75, 76
 Mathew, M., 120(118), 164(118), 189
 Matsumato, Y., 397(280), 398(280), 416

- Matsumoto, K., 151(341), 194
 Matsu-ura, Y., 120(342, 343), 122(342, 343), 194
 Mattes, R., 152(320), 194
 Matthews, G. N., 368(111), 412
 Matthys, P., 121(185), 191
 Mayne, N., 136(27), 151(230), 186, 192, 358(47), 410
 Mays, M. J., 171(326), 172(326), 194
 Medvedeva, A. V., 35(208), 68
 Medvedeva, V. G., 42(303), 72
 Meek, D. W., 217(133), 236
 Meerssche, M. van, 157(411), 196
 Meister, W., 240(77, 78), 241(77), 243(76, 80), 244(76), 245(76), 246(77, 79), 248(8), 251(76), 270, 271
 Melnikoff, A., 201(12, 13), 217(12, 13), 221(12, 13), 222(12, 13), 225(12), 233
 Merry, E., 170(334), 172(334), 194
 Meyer, K., 369(118), 399(281), 412, 416
 Meyer, T. J., 121(338), 183(287), 193, 194
 Mez, H. C., 379(171), 413
 Michealson, R., 106(45), 113
 Mischev, E. P., 35(208, 209, 210, 211), 68
 Midcalf, C., 157(298), 161(188, 299, 300), 162(188, 299, 300), 163(186, 188, 300), 191, 193
 Mikhailova, O. B., 66
 Mikheeva, V. I., 249(72), 271
 Miller, J. D., 116(347), 194
 Miller, J. R., 201(77, 103), 215(54, 97, 98), 217(77, 103, 104), 219(77), 221(77, 103), 222(77), 224(77), 234, 235, 371(127), 412
 Mills, O. S., 120(33, 38, 39, 40, 42), 126(33), 127(33, 40), 134(157), 137(39, 42), 153(42, 202), 157(38), 161(93), 162(349), 165(37, 348), 168(350), 187, 188, 189, 190, 191, 194, 195, 379(171), 397(236), 405(236), 413, 415
 Minacheva, M. Kh., 52(420), 77, 394(267), 395(267, 269), 396(269), 416
 Minamida, H., 136(387), 195, 196
 Minasyan, M. Kh., 53(430, 431, 432), 77, 371(132, 134), 384(213), 389(213), 412, 415
 Misono, A., 143(351), 165(351), 195
 Mitnacht, H., 364, 366, 368(114), 411, 412
 Moeller, C. W., 242(73), 271
 Moelwyn-Hughes, J. T., 117(352), 182(235), 192, 195
 Moerler, H. D., 169(368), 171(367, 368, 371), 172(368, 371), 195
 Moiseev, I. I., 371(137), 413
 Monchamp, R. R., 170(147), 172(147), 189
 Monerjan, A., 356, 410
 Montanari, F., 27(142), 65
 Moore, R. E., 239(104, 109), 243(104), 249(104, 109), 272
 Moreland, C. G., 89(72), 113
 Morris, W. F., 271
 Morrison, I. G., 81(34), 82(34), 112
 Mortikova, E. I., 395(268), 416
 Moser, E., 145(205, 206), 150(205, 206), 166(353, 354, 355, 356), 191, 195
 Motoyama, I., 104(70), 113
 Mozgova, K. K., 4(10), 60
 Müller, A., 369(118), 412
 Müller, J., 166(360), 170(212, 357, 358), 172(357, 358), 191, 195
 Müller, R., 366(100), 412
 Muettetietes, E. L., 397(237), 416
 Muller, E., 358(53), 411
 Muller, F. J., 142(431), 197
 Munro, J. D., 192
 Murahashi, S., 157(361), 191, 195, 396(275), 416
 Murata, H., 200(86, 105, 106), 235
 Murdoch, H. D., 52(428), 77
 Murray, R., 116(363), 117(363), 133(362), 195
 Musco, A., 200(43), 234

N

- Nad', M. M., 4(8, 17), 60
 Nagai, Y., 81(4), 102(4), 111
 Nagy, P. L. I., 182(235), 192, 371(128), 412

- Nakahara, A., 164(461), 197
- Nakamura, A., 120(390, 391), 122(391), 130(386), 131(390, 391), 135(394), 136(387), 153(393), 155(392), 156(392), 158(392), 159(389), 195, 196, 359(62), 411
- Nast, R., 169(368), 171(364, 365, 366, 367, 368, 369, 370, 371), 172(267, 364, 365, 368, 370, 371), 193, 195
- Natta, G., 116(114), 189
- Natta, R., 369(126), 412
- Nefedov, V. A., 399(286), 417
- Nefedova, M. N., 39(278, 279), 71, 81(36, 37, 48), 112, 113
- Nelson, J. H., 352(17), 410
- Nesmeyanov, A. N., 3(1), 4(2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13, 15, 16, 17, 18, 32), 5(4, 19, 20, 21, 22, 23, 24, 25, 26a), 6(30, 32), 7(33, 34, 35, 36, 37, 38, 39), 8(40, 42), 9(43, 44, 45, 46, 47, 48, 49), 10(50, 51, 52, 53, 54, 55), 11(55, 57), 12, 13(63, 64, 66, 67, 68, 69, 70, 71), 14(71, 72), 15(75, 76, 77, 78, 79), 16(78, 80, 81), 17(80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 92, 94, 95), 18, 19, 20(72, 96), 21(83, 87, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111), 22(115, 116), 23(116, 117, 119, 120), 24(122), 25(126, 127, 128, 129, 130, 131, 132, 133), 26(135, 136), 27(137, 138, 139, 140, 141), 28(143, 144, 145), 29(146, 147, 148, 149, 150), 30(136, 153, 154, 156, 157, 158, 159, 161, 162, 163), 31(146, 147, 148, 149, 156, 164, 165, 166, 170a), 32(150a, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176), 33(177, 178, 179), 34(180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205), 35(209, 210, 211, 212), 36(213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226), 37(227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247), 38(247, 248, 248a, 249, 250, 251, 252, 253, 254, 255, 256, 257, 261, 262), 39(253, 263, 264, 265, 272, 273, 274, 275, 276, 277, 278, 279), 40(280, 281, 282, 283, 284, 285, 287, 288, 289), 41(284, 285, 290, 291, 294, 295, 296, 297, 298, 299, 300), 42(292, 293, 298, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321), 43(321, 322, 323, 324, 325, 326), 44(327, 328, 329, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341), 45(342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353), 46(346, 347, 351, 354, 355, 356, 357, 358, 359), 47(360, 361, 362, 363), 48(364, 365, 366, 367, 368, 369, 373, 374, 375, 376, 377, 378), 49(372, 377, 379, 382, 383, 384, 385, 386, 388, 389, 390, 391), 50(392, 393, 394, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410), 51(406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419), 52(420, 421, 422, 423, 426), 53(433, 434, 435, 436, 437), 54(438, 439, 441), 55(442, 443, 444, 445, 446, 447), 56(448, 449, 450, 451, 452, 453, 454, 455), 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 81(37, 48, 49), 86(50), 87(50), 91, 92, 93, 103, 106, 107(22), 108, 109, 112, 113, 124(372), 125(373), 139(318), 183(374, 375, 376, 377), 195, 223(107, 108), 225(108), 226, 227(107), 230(108), 230, 235, 373(147), 374(158), 375(158, 160, 161), 376(161), 377(158), 378(161), 383(191), 384(201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212), 386(208, 209), 387(209), 388(212), 389(212), 394(265), 399(256, 257, 258, 259, 260), 407(251, 256, 257, 258, 259, 260), 408(260), 413, 414, 415, 416

Nesmeyanov, N. A., 104(31), 105(31), 112
 Nesmeyanova, O. A., 37(247), 38(247, 248), 69, 70
 Nicholas, L., 49, 75
 Nicolini, M., 180(452), 197
 Nicholls, B., 109(57), 113, 369(115), 412
 Nifant'ev, E. E., 31(165, 166), 66
 Nikiforov, A., 89(72), 113
 Nikitin, O. G., 39(276), 71
 Nikitina, T. V., 38(261), 40(282), 41(294, 295, 296), 42(319), 70, 71, 72
 Nikonova, L. A., 41(291), 42(301, 302, 308), 71, 72
 Nishido, T., 397(280), 398(280), 416
 Nitzmann, R. E., 222(14), 224(14), 225(14), 233
 Nixon, J. F., 153(379), 195, 358(48), 399(283), 410, 417
 Noack, K., 201, 222, 223(94), 224(109), 225(109), 226(109), 227(94), 228(109), 230(94, 109), 232(109), 235
 Nöth, H., 141(416a), 168(291, 381, 382, 416), 193, 195, 196, 240(75, 76, 77, 78, 81), 241(48, 77), 243(76, 80), 244(76), 245(74, 76), 246(77, 79), 248(8), 251(76), 269, 270, 271
 Nogina, O. V., 13, 23(117), 50(395, 396, 397, 398, 401, 402, 403, 406, 407, 408, 409, 410), 51(406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419), 62, 64, 76, 77, 384(201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211), 386(208, 209), 387(209), 414, 415
 Norburg, A. H., 168(380), 177(380), 180(380), 195
 Novikova, N. V., 9(47), 10(50, 53), 34(183, 184, 185, 186, 187, 189, 190, 193, 194, 195, 196, 198, 200, 205), 61, 62, 65, 67, 68
 Nowell, I. W., 142(72), 188
 Nugent, M. J., 108, 113
 Nyholm, R. S., 144(68), 178(89), 187, 188, 211(10), 212(10), 215(25), 233, 349, 358(54), 409, 411
 Nyman, F., 215(98), 235

O

Oberkirch, W., 371(135), 372(135, 138), 412, 413
 O'Brien, S., 372(143), 413
 Odaira, Y., 151(341), 194
 Öfele, K., 139(207, 208, 208a, 383), 166(383, 384), 191, 195
 Offhaus, E., 148(209), 163(209), 166(209), 191
 Ogawa, K., 159(384b), 195
 Okhlobystin, O. Yu., 21(109), 64
 Olah, G. A., 259, 271
 Olecowski, J. R., 399(282), 416
 Orchin, M., 351(9), 355(31a, 31b), 356(70, 71, 72), 357(40), 359(49), 360(71, 72), 361(75a, 75b, 77), 410, 411
 Oreshkin, I. A., 374(155), 413
 Orgel, L. E., 142(385), 143(297), 144(297, 339), 146(339, 340), 193, 194, 195, 201, 214, 215(112), 235, 378, 413
 Osborn, R. B. L., 135(232), 151(230), 153(231), 192
 Osborne, A. G., 215(113), 235
 Osipova, M. A., 9(47), 34(188, 197, 199), 61, 67
 Otsuka, S., 120(342, 343, 390, 391), 122(342, 343, 391), 130(386), 131(390, 391), 135(394), 136(387), 153(393), 155(392), 156(392), 158(392), 159(384b, 389), 194, 195, 196, 359(63), 411
 Ottley, R. P., 250(50), 262, 271
 Ovcharova, N. S., 8(42), 61
 Overend, J., 199, 235
 Owston, P. G., 120(278), 122(278), 193, 352(14), 410

P

Pachevskaya, V. M., 21(108, 110), 64
 Pässler, P., 169(61), 170(60, 61), 173(61), 174(61), 187
 Page, J. A., 98(59), 113
 Paiaro, G., 361(79), 411
 Palagyi, J., 123(395), 196
 Palazzi, A., 170(109), 173(109), 174(109, 109a), 185(109a), 188

- Palenik, G. J., 120(118), 164(118), 189
 Palm C., 397(240), 405(240), 415
 Pankowski, M., 217(114), 235
 Panova, V. A., 46(358), 74
 Panunzi, A., 361(79), 411
 Paquette, L. A., 140(399), 196
 Parker, D. J., 199(116), 211(115), 212
 (115, 116), 235
 Parker, V. B., 348(106), 272
 Parnell, K. H., 150(315), 194
 Parnes, Z. N., 23, 24, 64
 Parshall, G. W., 126(396, 397), 132, 133,
 196
 Parsons, T. D., 252(23, 102), 253(23),
 254(23), 257(23), 260(23), 266(23,
 102), 267(102), 270, 272
 Pasynskii, A. A., 37(230, 231, 232, 233,
 234), 56(451, 452, 453, 454, 456),
 69, 78, 346(270), 416
 Patel, C. G., 352(14), 410
 Patmore, D. J., 199(117), 215(117, 118),
 218(117), 235
 Paul, I., 199(50), 201(52), 209(93), 214
 (48), 215(4, 32, 33, 34, 35, 47, 48,
 49, 50, 51, 62, 91), 217(32, 92),
 218(52, 91), 219(87), 221(87), 222
 (87), 223(52), 226(52), 227(52),
 233, 234, 235
 Paul, I. C., 140(399), 196
 Pausacker, K. H., 399(285), 417
 Pauson, P. L., 81(34, 60), 82(34), 112,
 113, 118(400), 120(33), 121(214),
 122(214), 126(33), 127(33), 129
 (323), 132(34, 36), 134(157), 136
 (36), 137(34), 138(288, 289), 139
 (400, 401), 151(123), 157(35, 36,
 405), 158(215), 175(214), 187, 189,
 190, 191, 193, 194, 196, 397(246),
 406(246, 247), 415
 Pavlik, I., 407, 415
 Pearson, R. G., 348(1), 361(83), 367,
 379(102), 381(187), 409, 411, 412,
 414
 Pecherskaya, K. A., 23, 24(122), 25
 (122), 64
 Pecile, C., 180(452), 197
 Perevalova, E. G., 37(238, 247), 38(247,
 248, 254, 255, 256, 261), 39(265,
 272, 273, 279), 40(281, 282, 284, 285,
 286, 287, 288, 289), 41(284, 285, 294,
 295, 296, 297), 42(319), 43(325,
 326), 44(327, 329, 330, 331, 337,
 338, 339, 340, 341), 69, 70, 71, 72,
 73, 81(48), 90(20), 98(25), 99(62),
 107(22), 108(51, 61), 109(51, 61),
 112, 113, 383(191), 414
 Petrashkevich, I. A., 395(268), 416
 Petrosian, B. S., 26(135), 65
 Petrovskii, P. V., 32(176), 49(386), 51
 (413, 414, 419), 67, 75, 76, 77, 384
 (206, 207, 211) 407(251), 414, 415,
 416
 Petterson, L. L., 240(17), 244(18), 249
 (17, 18), 270
 Pettit, R., 109, 112, 409(261), 416
 Petz, W., 168(291, 416), 193, 196
 Petzovskaya, E. A., 32(176), 67
 Pflügmacher, A., 239(33), 270
 Pidcock, A., 364, 368(104), 370, 411, 412
 Pietropaolo, R., 358(50), 411
 Pignataro, S., 138(120), 189
 Pignolet, L. H., 381(183), 414
 Pilcher, G., 384(215), 415
 Pinkney, J. N., 161(301), 162(301), 163
 (301), 193
 Piper, T. S., 153(402), 170(402, 403),
 196, 394(263), 397(279), 416
 Piret, P., 120(404), 122(404), 157(411),
 175(404), 196
 Piron, T. S., 120(404), 122(404), 175
 (404), 196
 Pitcher, E., 199(119), 236
 Platzter, H. K., 170(261), 192
 Plesske, K., 101(63), 113, 383(194), 414
 Plowman, P. A., 52, 77
 Plyukhina, V. N., 42(310), 72
 Poddubnaya, S. S., 27(137, 140, 141),
 65
 Poë, A. J., 382(189), 414
 Pöllmann, P., 174(46, 48), 185(46), 187
 Poersch, F., 171(183), 173(183), 191
 Pohl, R. L., 169(167), 170(167), 190
 Pohland, E., 240(97), 292
 Poilblanc, R., 211(120), 236
 Poland, J. S., 127(325), 131(325), 194
 Poletti, A., 211(64), 234

Pollock, D. F., 379(174), 380(174), 381
(174), 414
Polovnyanyuk, I. V., 55(444), 56(450),
77, 78
Ponomarenko, A. A., 40(282), 71
Ponomarev, G. V., 396(270), 416
Ponomarev, S. V., 16(81), 17(81)
Porch, G. S., 5(25), 61
Portnova, S. L., 84(16), 87(16), 103(16,
17), 112
Post, E. W., 263, 271
Post, J. E., 358(51), 411
Postnov, V. N., 42(318, 321), 43(321),
72, 73
Potrosov, V. I., 10(51), 62
Potter, H., 17, 63
Powell, J., 372(140), 413
Praag, A. P., 361, 411
Pracejus, H., 24(124a), 64
Preston, F. J., 132(36), 136(36), 157
(36, 405), 187, 196
Pribytkova, I. M., 403(231), 415
Prinz, R., 141(406, 464), 196, 198
Prokof'ev, A. K., 42(308), 72
Pitsyna, O. A., 4(11, 14), 8(40, 41), 60,
61
Purcell, K. F., 143(407), 196
Pustyl'nik, Kh. P., 37(237), 69, 223
(107), 226(107), 227(107), 235
Pusyrev, V. P., 9(49), 61
Pyszora, H., 143(224), 192

Q

Qazi, A. R., 118(400), 138(289, 400,
401), 139(400, 401), 193, 196
Quarles, R. W., 246(83), 271
Quinn, H. W., 116(408), 144(408), 196

R

Ramey, K. C., 372(141, 142), 413
Ramsay, D. A., 205, 206(121), 207(121),
208(121), 236
Rausch, M. D., 83(65), 84, 88(71), 91
(71), 113, 364(90), 411
Reckziegel, A., 221(123), 236, 358(58),
359(58), 411

Reddy, M. L. N., 148(409), 196
Redhouse, A. D., 162(349), 165(348),
168(350), 194, 195
Reed, C. A., 154(243), 192
Reed, R. I., 132(36), 136(36), 157(36,
405), 187, 196
Reed, T. E., 148(409a), 196
Rees, C. W., 135(115), 137(115), 189
Reid, J. G., 215, 233
Reilly, C. N., 99(43, 44), 100(43, 44),
113
Reinboldt, H., 15, 62
Reinert, K., 242(44), 271
Reinheimer, H., 358(52), 411
Renk, I. W., 155(171a), 190
Reshetova, M. D., 44(331, 337), 73
Rest, A. J., 153(231), 192
Reutov, O. A., 4(11, 12, 13, 14, 15, 16),
5(26a), 8(40), 25(129), 26(135),
27(137, 138, 139, 140, 141), 40
(283), 60, 61, 65, 71, 106, 113
Reynolds, L. T., 98(66), 113
Rhee, I., 117(410), 118(229), 192, 196
Rheingold, A. L., 190
Ricci, J. S., 159(410a), 196
Richards, J. H., 81(26), 83(39), 102(26,
27), 107(26), 108, 112, 113
Richards, R. L., 165(32), 187
Richardson, D., 175(147a), 189
Rick, E. A., 173(25), 186
Ries, K., 170(268), 172(268), 193
Rigo, P., 171(92), 188
Rinehart, K. L., Jr., 96(67), 97, 113
Ritchey, W. M., 143(413), 144(413, 444),
146(413), 148(413), 171(444), 196,
197, 215(124), 236
Ritter, D. M., 247, 249(30, 85), 250(84),
251(84), 252(28), 253(84), 254(27,
28), 255(27), 256(27), 257(27, 84,
88), 258(84), 259(84, 87), 261(28,
86), 262(28), 268(28), 270, 271
Rivest, R., 144(276), 148(276), 193
Robertson, C. G., 120(112), 121(112),
173(81, 317), 174(112, 317), 188,
189, 194
Robinson, B. H., 201(77), 217(77), 219
(77), 221(77), 222(77), 224(77),
235

- Robinson, P. W., 201(77), 217(77), 219(77), 221(77), 222(77), 224(77), 235
- Robinson, S. D., 183(328), 194, 373(148), 413
- Robinson, W. R., 178(148), 190
- Rochev, V. Ya., 21(107), 110, 64
- Rockett, B. W., 138(401), 139(401), 196
- Rodionova, N. A., 42(320), 43(335, 336), 73
- Rodrique, L., 157(411), 196
- Rohm, W., 119(269), 193
- Rohmer, M., 171(369), 195
- Röhrscheid, F., 161(41), 187
- Rokhlina, E. M., 21(101, 107, 110, 111), 63, 64
- Roleff, H., 15, 62
- Romanenko, V. I., 42(292, 293, 307, 308, 315, 320, 321), 43(321, 324), 71, 72, 73
- Ronova, I. A., 384(214), 415
- Roos, H., 171(370), 172(370), 195
- Roper, W. R., 154(243), 178(322b), 183(322), 184(242), 185(322b), 192, 194
- Ros, R., 170(109), 173(109), 174(109, 109a), 185(109a), 188
- Rose, D., 150(224a), 192
- Rosen, H. M., 350(8), 410
- Rosenberg, H., 407(252, 253), 416
- Rosenberg, R., 239(110), 272
- Rosenblum, M., 90, 99, 102, 113, 263(89), 271, 407(248), 415
- Rosenfelder, J., 170(62), 187
- Rosenthal, A., 116, 122(412), 132, 196
- Ross, B. L., 143(413), 144(413, 444), 146(191, 413), 148(191, 413), 171(444), 191, 196, 197, 215(124), 236
- Ross, P., 378, 413
- Rossetti, R., 354(23), 355(23), 410
- Rossi, M., 359(63), 411
- Roundhill, D. M., 352(17), 410
- Rowe, G. A., 352(15), 353(15), 410
- Rubezhov, A. Z., 54(441, 442, 443), 77, 374(158), 375(158, 160, 161), 376(161), 377(158), 378(161), 384(212), 388(212), 389(212), 399(284), 400(284), 413, 415, 417
- Rubstov, M. V., 24, 64
- Rudenko, G. L., 17(82), 63
- Rudolph, R. W., 253(90), 254(90), 255(90), 256(90), 271
- Rühle, H., 140(210), 191
- Ruff, J. K., 168(414), 170(414), 178(414), 179(414), 196, 249(43), 270
- Ruffay, U., 358(52), 411
- Ruschmann, W., 240, 241(113), 272
- Rusholme, G. A., 173(338a), 185(338a), 194
- Russell, C. D., 98(28), 99, 112
- Russell, D. R., 142(72), 188
- Ruyter, E., 170(65), 187
- Ryan, R., 248(47), 271
- Ryang, M., 117(410), 118(229), 124(223), 192, 196
- Rybin, L. V., 28(145), 31(170a), 32(150a, 171, 172, 173, 174, 175), 33(177, 178, 179), 34(180), 65, 66, 67
- Rycheck, M., 357(40), 361(75b), 410, 411
- Rybinskaya, M. I., 28(143, 144, 145), 29(146, 147, 149, 150), 30(158, 159, 161, 162, 163), 31(146, 147, 149, 164), 32(150a, 167, 168, 169, 170, 170a, 171, 172, 173, 174, 175, 176), 34(180), 65, 66, 67

S

- Sacher, R. E., 153(247), 154(247), 192
- Sadasivan, N., 163(26), 164(216), 191
- Saha, H. K., 253(91), 254(91), 255(91), 265(91), 271
- Sakai, S., 373(151), 413
- Sakamaki, K., 145(459), 197
- Samuel, A. A., 171(283), 193
- Sanders, A. P., 99(43, 44), 100(43, 44), 113
- Sanders, J. R., 125(237), 126(236), 192
- Sandhu, M. A., 81(34, 60), 82(34), 112, 113
- Sandir, R. B., 6, 7, 61
- Santer, J. O., 102(69), 113
- Sappa, E., 354(23), 355(23), 410
- Sato, M., 104(70), 113
- Sauerborn, H., 170(58a), 187
- Sauter, J. O., 407(248), 415

- Savel'eva, I. S., 34(188, 204), 67, 68
 Sawodny, W., 248(8), 270
 Saxby, J. D., 144(68), 187
 Sazonova, N. S., 41(299), 42(309, 310), 43(322), 72, 73
 Sazonova, V. A., 9(44), 15(75, 76), 17(94, 95), 38(262), 41(291, 298, 299, 300), 42(292, 298, 300, 301, 302, 303, 304, 305, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 320, 321), 43(321, 322, 323, 324), 44(334, 335, 336), 48(378), 61, 63, 71, 72, 73, 75
 Schachtschneider, J. H., 78, 413
 Schächl, H., 174(46, 48), 185(46), 187
 Schaeffer, R., 265(34), 270
 Schell, H., 369(121), 412
 Schick, H., 243(80), 269, 271
 Schier, E., 118(49), 187
 Schindler, H. D., 170(64), 171(63, 101a), 187, 188
 Schirawski, G., 170(73), 188
 Schlesinger, H. I., 239(38, 104, 109), 242(92), 243(104), 249(104, 109), 250(38, 105), 252(23, 102), 253(23), 254(23), 257(23, 92), 260(23), 265(92), 266(23, 102), 267(102), 270, 272
 Schlögl, K., 132(44), 138(415), 187, 196
 Schmid, G., 141(416a, 416b), 168(291, 381, 382, 416), 193, 195, 196
 Schmidt, E., 171(101a), 188
 Schmidt, P. J., 351(9), 355(31a, 31b), 361(75a, 77), 410, 411
 Schmidtke, H. H., 177(417), 196
 Schmutzler, R., 358(55, 56), 411
 Schneider, R. J., 170(211, 212, 213), 172(211), 191
 Schönleber, D., 400(288), 417
 Schomaker, V., 379(170), 413
 Schonauer, G., 148(440), 197
 Schrägle, W., 240(81), 271
 Schram, E. P., 250(93, 103), 272
 Schrauzer, G. N., 145(222, 418, 419), 146(419), 191, 196
 Schro'en, H., 369(119), 412
 Schropp, W., 169(270), 170(270), 193, 397(243, 244), 406(243, 244), 415
 Schrumb, W. C., 239(94), 272
 Schubert, E. H., 144(420), 196
 Schuierer, E., 176(51), 187
 Schulz, H., 171(371), 172(371), 193, 195
 Schumm, R. H., 248(106), 272
 Schuster, L., 121(271), 170(271), 193
 Schwab, R., 178(66), 179(66), 187
 Scollary, G. R., 178(139), 189
 Seeholzer, J., 369(122), 412
 Seel, F., 118(421), 196
 Seifert, F., 383(198), 414
 Self, J., 248(42), 270
 Semin, G. K., 21(106, 109, 111), 51(415), 64, 76
 Semion, V. A., 55(445), 78
 Seshadi, K. S., 199, 204(125), 223(125), 224(125), 231(125), 236
 Setkina, V. N., 39(277, 278, 279), 40(280), 49(382, 383, 384), 71, 75, 81(36, 37, 48, 49), 112, 113, 393(226), 415
 Severin, E. S., 30(154), 66
 Sexton, M., 358(48), 410
 Seyferth, D., 144(290), 193
 Seyffert, H., 169(462), 170(462), 171(462), 197
 Sharaev, O. K., 374(155), 413
 Sharpe, A. G., 168(122), 189
 Shatalov, H. V., 384(202), 414
 Shaw, B. L., 178(124), 183(330), 189, 194, 352(16), 372(140), 373(148), 410, 413
 Shaw, B. W., 406(247), 415
 Shchembelov, G. A., 183(377), 195
 Shearer, H. M. M., 162(422), 163(422), 196, 379(171), 413
 Sheats, J. E., 88(71), 91(71), 113
 Sheinker, Yu. N., 37(229, 237), 41(290), 50(391, 392), 51(416), 69, 71, 75, 76, 84(16), 87(16), 103(16, 17), 112, 223(107, 108), 225(108), 226(107), 227(107), 230(108), 232(108), 235
 Sheline, R. K., 141(427), 142(172), 143(187, 427, 469, 471), 144(420, 469), 145(469, 471), 148(172, 173, 428, 471), 149(469), 190, 191, 192, 196, 198, 215(126, 127, 128, 129), 236, 350(6), 409

- Shembelov, I. A., 53(434), 77
 Shen, L. M. C., 89(72), 113
 Shenkin, P. S., 83(77, 78), 84(77), 85(77), 87(77), 114
 Shilov, A. E., 116(87), 488
 Shilovtseva, L. S., 38(255), 40(282), 43(325, 326), 45(343), 46(356, 357, 358, 359), 70, 71, 73, 74, 92(56), 113, 399(260), 407(260), 408(260), 416
 Shore, S. G., 240(21), 243(111), 253(112), 270, 272
 Shriver, D. F., 143(441), 168(423), 196, 197, 240(10), 269(10, 95), 270, 272
 Shubkin, R. L., 149(446), 177(446), 197
 Shupack, S. J., 356(71, 72), 360(71, 72), 411
 Shustorovich, E. M., 384(199), 414
 Shwedova, G. N., 34(205), 68
 Siegel, A., 83(65), 84, 113
 Siekman, R. W., 404(232), 415
 Silver, H. B., 240(20), 270
 Sim, G. A., 120(112), 121(111, 112), 173(317), 174(110, 112, 317), 175(110, 111), 188, 189, 194
 Simmons, H. D., 139(201), 144(201), 191
 Simons, P. B., 215(76), 234
 Singer, H., 169(424), 171(424), 183(424), 196
 Singh, A., 199(5), 233
 Singh, M. M. (*also* Singkh, M. M.), 178(241, 425), 183(241), 192, 197
 Sinha, A. I. P., 168(380), 177(380), 180(380), 195
 Sirotkina, E. I., 45(346, 347, 351, 352), 46(346, 347, 351, 355), 74, 86(50), 87(50), 113, 404(233), 415
 Skinner, H. A., 384(215), 415
 Skripkin, V. V., 37(228), 69
 Sleeser, P. D., 376(162), 413
 Sloan, H., 211(28), 233
 Sloan, T. E., 177(426), 178(426), 197
 Slocum, D. W., 80(75), 81(75), 83(75, 76, 77, 78), 84(73, 74, 75, 77), 85(77), 87(77), 94(79), 113, 114
 Slonimskii, G. L., 28(145), 65
 Sly, W. G., 354(24), 410
 Smedal, H. S., 173(50, 52, 338a), 174(52), 185(338a), 187, 194, 215(15), 233
 Smidt, J. D., 368(104), 370, 412
 Smirnov, V. N., 199, 231(65a), 234
 Smirnova, S. A., 40(288), 71, 99(62), 113, 392(221), 402, 415
 Smith, A. E., 371(130), 412
 Smith, D. C., 116(363), 117(363), 195
 Smith, J. G., 214(48), 215(47, 48, 49), 219(48), 234
 Smithies, A. C., 357(40), 410
 Smolina, T. A., 24, 64
 Sneen, R. A., 24, 64
 Sokolov, S. D., 31(170a), 66
 Sol'nikova, G. P., 43(324), 23
 Sonogashira, K., 139(201), 144(201), 191
 Sowerby, J. D., 162(422), 163(422), 196
 Spatalov, G. V., 50(408), 57(408), 76
 Sperber, V., 118(421), 196
 Stahl, H. O., 397(278), 416
 Stahl, R., 201(12, 13), 217(12, 13), 221(12, 13), 222(12, 13), 225(12), 233
 Stamper, P. J., 209(93), 215(32, 33, 34, 35), 217(32), 233, 234, 235
 Stanghellini, P., 354(25), 410
 Staricco, E., 66(99), 412
 Statton, G. L., 372(141, 142), 413
 Steele, D., 199, 236, 248(37), 270
 Steinrücke, S., 371(135), 372(135), 412
 Stenson, J. P., 151(447), 161(449), 167(448), 197
 Stiddard, M. H. B., 121(274), 178(274), 193, 199(116), 200(22, 24), 211(115, 116), 212(115, 116), 215(23, 113), 233, 235, 368(112), 412
 Stock, A., 237(96), 239(96), 240(97), 272
 Stolz, I. W., 141(427), 142(172), 143(427), 148(172, 173, 428), 190, 197, 215(126, 127, 128, 129), 236, 350(6), 409
 Stone, F. G. A., 52, 77, 116(1, 2), 127(150, 151), 131(346), 133(97, 98), 135(232), 136(27), 137(98), 140(99, 100, 152, 153, 233), 144(219), 151(99, 100, 230), 153(231), 186, 188, 190, 191, 192, 194, 199(50, 119,

- 134), 201(52), 210(6), 214(48), 215
(4, 47, 48, 49, 50, 51, 62), 218(52),
223(52), 226(52), 227(52), 233,
234, 236, 253(29), 265(34), 270,
357(39), 358(47, 57), 359(57, 64),
379(172), 397(276), 406(242), 410,
411, 413, 415, 416
- Storhoff, B. N., 149(429), 150(429), 197
- Stranks, D. R., 348(2), 409
- Streith, J., 140(430), 197
- Strickland, R. C., 108(6), 112
- Strohmeier, W., 141, 142(431, 432, 436),
144(433), 146(250), 148(250, 437,
439, 440), 149(432, 434, 438), 192,
197, 364, 366(99, 100), 368(114),
383(197, 198), 411, 412, 414
- Struchkov, Yu. T., 13(6), 53(430, 431,
432), 54(438), 55(445), 62, 77, 371
(132, 134), 384(213), 389, 412, 415
- Stubbs, W. H., 138(289), 193, 397(246),
406(246, 247), 415
- Su, R. S., 159(440a), 160(440a), 197
- Sumida, S., 397(280), 398(280), 416
- Sun, J. Y., 129(137), 175(37), 176(137),
189
- Surtess, J. R., 129(155), 190
- Swain, J. R., 153(379), 195
- Swanson, B., 143(441), 197
- Swindell, R. T., 108(6), 112
- Swoboda, P., 176(51), 187
- T**
- Tacchi, Venturi, M., 169(70), 171(70),
187
- Takahashi, Y., 373(151), 413
- Tanaka, K., 371(135, 136), 372(135),
412, 413
- Tate, D. P., 143(443), 144(443, 444),
146(443), 148(442), 171(444), 197
- Taunton-Rigby, A., 140(233), 192, 359
(64), 411
- Taurkan, P. A., 4(13), 60
- Taylor, B. W., 364, 368(104), 370, 411,
412
- Taylor, F. B., 246, 264(51), 271
- Taylor, K. A., 116(117), 189
- Taylor, M. B., 140(84, 85), 151(84, 85),
188
- Temkin, O. N., 352, 353, 410
- Teyssié, P. H., 359(65), 411
- Theophanides, T., 353, 410
- Thiers, M., 145(121), 189
- Thomas, J. C., 142(445), 171(445), 172
(445), 197
- Thompson, D. T., 116(117), 184(116),
189, 355(29), 410
- Thompson, J. A. J., 215(76, 131), 231,
234, 236
- Thompson, N. R., 252(68), 271
- Thorp, R., 163(26), 164(216), 191
- Thorpe, C. A., 163(186), 191, 193
- Tilney-Bassett, J. F., 397(236, 237, 238,
239), 405(236, 237, 238, 239), 415
- Timms, P. L., 239(98, 99), 272
- Tinyakova, E. I., 371(137), 374(155), 413
- Tirouflet, J. C., 98(35), 112
- Tishler, M., 17, 63
- Tobe, M. L., 349, 409
- Todd, P. F., 120(278), 122(278), 193
- Tolstaya, T. P., 4(18), 5(4), 7(30, 33,
34, 35, 36, 37, 38, 39), 8(40, 42),
24(122), 25(122) 60, 61, 64
- tom Dieck, H., 148(170), 149(170, 171),
151(74, 75), 152(75, 76, 169), 155
(77, 79, 168, 171a), 164(76, 78),
188, 190
- Torii, A., 159(38, 46), 195
- Toropova, E. M., 5(20), 60
- Trahanovsky, W. S., 109(81), 114
- Trefonas, L., 248(100), 272
- Treichel, P. M., 149(446), 151(447),
161(449), 167(448), 177(446, 450),
178(450), 179(450), 197
- Tripath, J. B. P., 217(132), 236
- Trofimenko, S., 128(451, 451a), 197
- Truter, M. R., 144(331), 194
- Tsai, J. H., 116(408), 144(408), 196, 215
(36), 234
- Tsang, W. S., 217(133), 236
- Tsurgozen, L. A., 49(388), 75
- Tsutsumi, S., 117(410), 118(229), 124
(223), 151(341), 192, 194, 196
- Tucker, P. M., 215(62), 234, 265(34),
270

Tucker, S. P., 94(79), 114
 Turco, A., 171(92), 180(452), 188, 197
 Turgin, K. F., 50(392), 75
 Turin, V. O., 43(326), 73
 Turner, R. W., 366(97), 412
 Tvorogov, A. N., 21(113), 64

U

Uchida, Y., 143(351), 165(351), 195
 Ueki, T., 120(342, 343), 122(342, 343), 194
 Ugo, R., 151(453, 454), 160(82, 83), 188, 197
 Uguagliati, P., 358(50), 366(101), 411, 412
 Ulm, K., 346(272), 416
 Ul'yanova, T. N., 37(227, 236), 69
 Urch, D. S., 250(69), 252(68), 371
 Urry, G., 237(101), 239(101, 104), 242(92), 243(104), 249(104), 250(93, 102), 251(101), 252(23, 107), 253(23, 91), 254(23, 91), 255(91), 257(23, 92, 101), 260(23), 265(91, 92, 101), 266(23, 102), 267(102), 270, 271, 272
 Ustynyuk, N. A., 55(447), 78, 125(373), 195, 401(227, 228), 415
 Ustynyuk, Yu. A., 32(171, 172, 173, 174, 175), 33(177, 178), 41(297), 43(325), 44(327, 328, 329, 330, 338, 339, 341), 53(433, 434, 437), 56(449), 66, 67, 71, 72, 73, 77, 78, 86(50), 87(50), 113, 183(377), 195, 393, 398(225), 399(225), 401(227), 402(225), 403(231), 404, 415
 Uttech, R., 371(131), 412
 Uvstigneeva, R. P., 396(270), 416

V

Vaglio, G., 354(25), 410
 Vainberg, A. M., 53(437), 77
 Vallarino, L., 197
 Valueva, Z. P., 35(210, 211), 48(373, 374, 375, 376), 68, 75
 Van Bronswijk, W., 178(89), 188, 215(25), 233

Van der Akker, M., 393(224), 398(224), 415
 Vander Kelen, G. P., 141(165), 148(165), 190
 Van Meerssche, M., 120(404), 122(404), 175(404), 196
 Van-Shi-Khun, 34(202), 68
 Varshavskii, Yu. S., 136(457), 178(241, 425), 183(241), 192, 197
 Vasil'eva, E. I., 17(95), 63
 Vaska, L., 197
 Vastine, F., 129(137), 175(137), 176(137), 189
 Veazey, R. L., 108(6, 7), 112
 Venanzi, L. N., 169(127), 170(127), 189, 353(19), 355, 410
 Venerable, D., 163(217), 164(217), 191
 Vereshchagina, N. I., 15(77), 63
 Vignollet, Y., 85(82), 114
 Vil'chevskaya, V. D., 13(64), 25(130), 34(182), 38(253), 39(253, 263, 264), 62, 65, 67, 70
 Vitt, S. V., 38(257), 70
 Voevodskaya, T. I., 401(227), 403(231), 415
 Vogel, M., 171(101a), 188
 Vogl, J., 170(67), 187
 Volger, H. C., 361, 372(146), 373(146), 411, 413
 Vol'kenau, N. A., 25(131, 132), 38(252, 253), 39(253), 44, 45(342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353), 46(346, 347, 351, 354, 355, 356, 357, 358, 359), 65, 70, 73, 74, 86(50), 87(50), 113, 399(256, 257, 258, 259, 260), 407(256, 257, 258, 259, 260), 416
 Volkenau, N. S., 91(53), 92(55, 56), 93(54), 113
 Volkov, V. L., 35(208, 210, 211), 68
 von Egidy, A. I., 248(46), 271
 Vrieze, K., 361, 372(146), 373(146), 411, 413

W

Wade, K., 379(169), 413
 Wagman, D. D., 248(106), 272
 Wailes, P. C., 190
 Wakamatsu, H., 145(459), 197

- Walker, J. A., 248(32), 270
Walker, S. M., 253(24), 270
Wallis, J. W., 143(224), 192
Wallwork, S. C., 178(273), 193
Walter, D., 371(135), 372(135, 144), 412, 413
Walton, R. A., 142(460), 143(460), 178 (148), 190, 197
Wang, J. H., 164(461), 197
Wang, T. S., 368(111), 412
Wannagat, U., 169(462), 170(73, 462), 171(462), 188, 197
Ware, M. J., 215(98), 235
Wartik, T., 239(104, 109, 110), 242(63), 243(104, 107, 108), 247(41), 249 (104, 109), 250(105), 253(118, 120), 254(118), 255(118), 256 (120), 260(120), 263(39), 264(2), 266(39), 267(119), 269, 270, 271, 272
Warren, L. F., 384(212a), 392(212a), 415
Warreni, J. D., 365(95), 412
Watanabé, Y., 159(384b), 195
Waters, W. A., 6, 61
Watts, W. E., 81(34, 60), 82(34), 112
Weil, T. A., 361(77), 411
Weiss, E., 52(428), 77
Weiss, R., 156(160), 190
Weissman, S. I., 250(103), 272
Welch, C. N., 243(111), 253(112), 272
Wells, D. K., 109(81), 114
Wender, I., 116, 122(412), 132, 196
Wenzl, R., 140(245), 192
West, C., 106(15), 112
Werner, H., 52(425), 77, 141(162, 163, 406, 464), 166(256), 173(52, 463, 463a), 174(52, 463), 183(463), 185 (463a), 190, 192, 196, 197, 198, 215 (15), 233, 373(152), 381(184), 413, 414
Wharton, B. J., 400(290), 417
Wheatley, P. J., 248(5), 269
Whiteley, R. N., 125(237), 192
Whiting, M. C., 109(57), 113, 369(115), 412
Whyman, R., 178(148), 190
Wiberg, E., 240, 241(113), 272
Wickham, A. J., 171(240), 192
Wild, S. B., 139(201), 144(201), 191
Wiles, M. R., 148(409), 196
Wilford, J. B., 199(134), 236
Wilke, G., 358(53), 371(135, 136), 372 (135, 144, 145), 373, 411, 412, 413
Wilkins, R. G., 362, 411
Wilkinson, G., 98(59, 66) 113, 119 (139a), 150(224a), 153(402), 169 (424), 170(402, 403), 171(239, 326, 424), 172(239), 178(327), 183 (424), 189, 192, 194, 196, 199(5, 42), 200(42), 201(42), 233, 234, 359(59), 383(193), 394(263), 397 (279), 411, 414, 416
Willcockson, G. W., 252(115), 272
Williams, A. A., 352(15), 353(15), 410
Williams, D. H., 95(10), 112
Williams, L. E., 180(107), 188
Williamson, J. M., 192
Wilmarth, W. K., 242(73), 271
Wilson, E. B., 201(135), 202(135), 203 (135), 213(135), 218(135), 236
Wilson, R. J., 384(212a), 392(212a), 415
Wing, R. M., 162(148a), 190, 200(44, 45), 201(136), 217(136), 220(136), 221(136), 223(136), 230(136), 234, 236
Winch, B. L., 54, 77, 384(212), 388(212), 389(212), 415
Winscomb, C. J., 400(290), 417
Winstein, S., 355(35), 376(162), 410, 413
Winternitz, P. F., 242(116), 272
Winterton, N., 183(287), 193
Witanowsky, M., 85(82), 114
Wojcicki, A., 159(440a), 160(440a), 169 (280, 281), 170(280, 281), 177(193, 194, 279, 426, 465), 178(193, 194, 426, 465, 466), 179(279), 180(280, 281), 181, 186, 191, 193, 197, 198, 207(77), 215(65), 217(27, 133), 219(77), 221(77), 222(77), 224 (77), 234, 235, 236, 381(188), 390 (188), 414
Wolkenstein, N., 210(55, 56), 234
Wonniger, P., 170(334), 172(334), 194
Wood, J. L., 200(137), 236
Wotiz, J. H., 368(111), 412

Wu, T. K., 83(83), 114
 Wustrow, W., 15, 62

Y

Yachontov, L. N., 24(124), 64
 Yagupsky, G., 200(43), 234
 Yakovlev, V. A., 374(155), 413
 Yamamoto, Y., 151(468), 161(467), 198,
 397(245), 404(245), 415
 Yamazaki, H., 151(468), 161(467), 198,
 368(105), 397(280), 398(280), 412,
 416
 Yang, M. T., 124(181), 190
 Yasuoka, N., 120(342, 343), 122(342,
 343), 184
 Yoshida, T., 120(342, 390, 391), 122
 (342, 391), 131(390, 391), 135(394),
 153(393), 155(392), 156(392), 158
 (392), 159(384b, 389), 194, 195,
 196
 Young, M. T., 124(182), 190
 Young, R. C., 170(147), 172(147), 189
 Young, W. G., 376(162), 413
 Yur'eva, L. P., 39(265, 272, 273, 276),
 40(289), 41(290), 44(333), 70, 71,
 73, 103(17), 112

Z

Zacharova, M. Ya., 36(215, 217), 37
 (235), 68, 69
 Zanzottera, C., 169(70), 171(70), 187
 Zeidler, A., 121(272), 193
 Zeldin, M., 253(117, 118, 120), 254
 (118), 255(117, 118), 256(117,
 120), 257(117), 260(120), 266
 (117, 119), 267(117, 119), 272
 Zharikova, N. A., 40(285), 41(285), 71,
 108(61), 109(61), 112, 401(227),
 415
 Zhukov, A. P., 21(106), 64
 Ziegler, M. L., 143(469, 471), 144(469,
 470), 145(469, 471), 148(471), 149
 (469), 198
 Zimmermann, H., 371(135), 372(135),
 412
 Zingales, F., 363(87, 88), 366(101), 367,
 411, 412
 Zlotina, I. B., 47(362, 366, 367, 368), 48
 (369), 49(379, 383, 384), 74, 75,
 139(378), 195
 Zol'nikova, G. P., 42(321), 43(321), 53
 (437, 438), 73, 77
 Zudkova, G. I., 44(334, 335), 73
 Zwolenik, J. J., 239(71), 271

Author Index¹

Reviews of Organo-Transition Metal Chemistry 1950–1970

A

Abbate, F. W., 25.30
Abel, E. W., 5.2, 5.3, 8.1, 14.1
Adamson, A. W., 33.1
Aguiló, A., 28.1
Allen, A. D., 42.1
Anderson, J. S., 6.1
Andrews, L. J., 19.4
Angelici, R. J., 27.1
Anisimov, K. N., 4.14, 10.2
Anker, M. W., 9.9
Antonova, A. B., 10.2
Arakawa, K., 25.1
Ariyoshi, J., 15.21, 29.27
Armer, B., 4.37

B

Baay, Y. L., 10.3
Babitskii, B. D., 20.4
Baddley, W. H., 17.1
Baird, M. C., 11.1
Bald, J. F., 10.3
Basolo, F., 27.2, 27.4
Bebb, R. L., 25.12
Beck, W., 5.5, 7.2
Beermann, C., 30.1
Belluco, U., 19.5
Bénard, J., 5.4
Bennett, M. A., 19.1, 23.1
Berger, M. N., 30.2
Bernhauer, K., 34.1
Berry, A. D., 10.3
Bestian, H., 30.1, 30.3, 30.4
Beverwijk, C. D. M., 4.36
Bier, G., 30.5
Bigorgne, M., 5.4
Bikales, N. M., 30.6
Bird, C. W., 28.2
Birkenstock, U., 29.1

Birmingham, J. M., 22.4, 22.5, 25.28
Biryukov, B. P., 11.2
Bittler, K., 28.3
Blanchard, A. A., 6.2, 6.3, 6.4
Bland, W. J., 16.1
Blase, S., 41.2, 41.3
Bocard, C., 31.3
Bogdanovic, B., 20.6, 28.4, 28.33, 29.1
Bonati, F., 14.2, 14.3
Bond, G. C., 29.2, 29.3, 29.4, 29.5
Bönnemann, H., 29.1
Bonnert, R., 34.2
Boocock, G., 30.2
Booth, G., 13.1
Borod'ko, Y. G., 42.2
Bottomley, F., 42.1, 42.3
Rowden, F. L., 19.18
Bradley, D. C., 2.1, 2.19
Brandenberger, H., 41.1
Braun, D., 25.2
Braun, G., 7.2
Bregadze, V. I., 2.17, 32.5
Brown, D. A., 27.3, 35.1, 35.2, 35.3
Bruce, M. I., 4.20, 7.1, 16.2, 16.3, 38.1
Bublitz, D. E., 25.3
Bulkin, B. J., 11.3
Burg, A. B., 13.2
Burmeister, J. L., 27.4
Büttner, W., 42.4

C

Cable, J. W., 35.4
Cais, M., 25.4, 25.5, 38.2
Carra, S., 29.6
Cassar, L., 28.6
Cenini, S., 31.9
Cesca, S., 30.13
Chalk, A. J., 4.23, 29.7
Chambers, D. B., 38.3

¹Author Index for appendix (pp. 297–346) to the article "Organo-Transition Metal Chemistry—A Guide to the Literature 1950–1970" by M. I. Bruce.

- Chambers, R. D., 16.4
 Chatt, J., 4.38, 9.1, 9.2, 15.1, 31.1, 42.5
 Chini, P., 11.4, 11.5
 Chiusoli, G. P., 28.5, 28.6
 Chivers, T., 16.4, 17.2
 Churchill, M. R., 23.2, 40.1, 40.2
 Clark, H. C., 16.5
 Clauss, K., 30.3, 30.4
 Cleare, M. J., 43.1
 Cohen, S. C., 16.6
 Collman, J. P., 29.8, 29.9, 31.2, 32.1
 Colton, R., 9.9
 Cordes, J. F., 2.15
 Cotton, F. A., 11.6, 15.2, 22.3, 24.2, 24.3
 Coutts, R. S. P., 4.2
 Cramer, R., 29.10
 Criegee, R., 21.1, 21.2
 Crociani, B., 19.5
 Cross, R. J., 4.30, 15.3
 Crosse, B. C., 14.1
 Cullen, W. R., 16.2, 16.7
 Czakis-Sulikowska, M., 11.7
- D**
- Dall'Asta, G., 30.13
 Davies, N. R., 29.11
 Davydov, V. N., 29.12
 Dawans, F., 30.7
 Dehnert, J., 3.1
 Dobson, G. R., 12.1
 Dyatkin, B. L., 1.15
 Dyatkina, M. E., 35.5
- E**
- Ehntholt, D. J., 18.2, 19.6
 Ehrlich, K., 19.6
 Eichler, S., 28.22
 Eisch, J. J., 2.2
 Elmes, P. S., 13.3
 Emerson, G. F., 19.6, 19.15, 19.16
 Engelmann, T. R., 25.36
 Ernst, C., 25.36
 Eschenmoser, A., 34.3
- F**
- Falk, H., 25.6
 Fedorov, L. A., 20.1
 Fergusson, J. E., 4.17, 42.6
 Fischer, E. O., 19.7, 20.2, 22.1, 22.6, 22.9
 Fleischer, P. D., 33.1
 Fong, C. W., 31.7
 Ford, P. C., 42.7
 Fottrell, P. F., 42.8
 Franck, J. P., 31.3
 Freidlina, R. K., 1.1
 Fritz, H. P., 22.1, 22.9, 36.1
 Fujiwara, Y., 28.16
- G**
- Gamlen, G. A., 2.3, 2.4
 Gansheimer, J., 4.13
 Garnett, J. L., 29.13
 Garnovskii, A. D., 39.2
 Giannini, U., 30.13
 Gibson, D., 15.4
 Giering, W. P., 19.6
 Gilman, H., 1.2, 2.2, 3.2
 Ginsberg, A. P., 9.3
 Giraitis, A. P., 2.21
 Glockling, F., 38.3
 Glockner, P., 28.22
 Gol'danskii, V. I., 39.1
 Golubeva, I. A., 25.39
 Gondal, S. K., 10.3
 Green, M. L. H., 9.4, 9.5, 9.6, 20.3
 Grevels, F.-W., 33.2
 Griffith, W. P., 4.22, 43.2
 Gubin, S. P., 39.3
 Gupta, V. D., 14.7
 Gusev, A. I., 40.3
 Guy, R. G., 19.2
 Gysling, H., 4.1
- H**
- Haas, M. A., 32.2
 Hafner, W., 28.23, 28.24
 Hagen, A. P., 10.3
 Hagihara, N., 2.5, 3.4, 4.18, 15.5, 18.1, 28.7, 28.8, 28.9, 28.10
 Haines, L. M., 36.2
 Halpern, J., 29.14, 29.15, 29.16, 31.4
 Hancock, M., 15.21
 Harasawa, K., 2.6
 Hardt, P., 20.6
 Harrod, J. F., 4.23
 Hartley, F. R., 4.31, 19.3
 Hashimoto, H., 15.6, 28.11, 29.30

Hawthorne, M. F., 26.1, 26.2, 26.3
 Hayter, R. G., 12.2
 Heck, R. F., 4.24, 15.7, 15.8, 31.5
 Heimbach, P., 20.6, 28.4, 28.12, 28.33
 Hein, F., 1.3, 2.7, 6.16
 Henrici-Olivé, G., 30.8, 42.9
 Herzog, S., 3.1, 36.5
 Hester, R. E., 36.3
 Hidai, M., 4.19, 4.21, 4.25, 42.17
 Hieber, W., 1.4, 5.5, 6.5, 6.6, 6.7, 7.2
 Hileman, J. C., 5.6
 Ho, T., 42.10
 Hoggarth, E., 2.8
 Howard, R. N., 30.2
 Huang, Y. T., 28.13
 Hubert, A. J., 29.17
 Huggins, D. K., 36.4
 Hüttel, R., 4.32, 4.33

I

Ioffe, S. T., 1.15
 Ioganson, A. A., 4.14
 Imai, H., 25.8
 Inoue, S., 30.9
 Ishii, Y., 31.6
 Ishino, T., 4.3
 Itoh, K., 31.6

J

Jacque, L., 4.11
 Jaluvka, J., 5.7
 James, B. R., 29.18
 James, D. W., 36.7
 Jahn, W., 10.1
 Jennings, C. A., 25.36
 Jensen, H., 30.4
 Jensen, K. A., 19.8
 Jira, R., 28.23, 28.24
 Johnson, B. F. G., 38.4, 43.3
 Jolly, P. W., 28.12
 Jones, D. J., 9.6
 Jones, R., 19.9
 Jones, R. G., 3.2
 Jones, W., 25.36

K

Kabachnik, M. I., 1.1
 Kaden, R., 41.1, 41.2, 41.3

Kaes, H. D., 2.9, 36.4, 37.2
 Kawaguchi, S., 22.10
 Kersaint, G., 4.11
 Keller, H. J., 37.1
 Keller, R. N., 6.17
 Kerber, R. C., 18.2
 Keim, W., 20.6
 Khrapov, V. V., 39.1
 Kindler, H., 28.31
 King, R. B., 7.3
 Kitching, W., 31.7, 32.3, 32.4
 Koerner von Gustorf, E., 33.2
 Kojer, H., 28.23
 Kolobova, N. E., 4.14, 10.2
 Kolomnikov, I. S., 29.29
 König, E., 36.5
 Koonsivitsky, B., 25.36
 Kopp, E. L., 30.10
 Kormer, V. A., 20.4
 Körner, H., 41.1, 41.2, 41.3
 Korshak, V. V., 1.1
 Kotegov, K. V., 4.15
 Kotz, J. C., 35.6
 Koyano, T., 29.27
 Kragten, J., 35.7
 Krentsel', B. A., 30.17
 Kritskaya, I. I., 15.9
 Kröner, M., 20.6, 28.33
 Kruck, T., 13.4
 Kruglaya, O. A., 10.7
 Kuchynka, K., 42.11
 Kukina, G. A., 40.4
 Kumada, M., 2.10, 25.9
 Kursanov, D. N., 25.35
 Kuznetsov, V. I., 1.15
 Kuznik, B., 11.7
 Kwiatek, J., 29.19

L

Lappert, M. F., 2.11, 15.10
 Latyaeva, V. N., 4.4, 15.5
 Lautsch, W. F., 41.1, 41.2, 41.3
 Lehmann, H.-M., 41.1
 Lehne, M., 6.8
 Leusink, A. J., 4.36
 Lever, A. B. P., 19.18
 Levy, M. N., 15.21, 29.27
 Lewis, J., 11.8, 11.9, 38.4, 43.4, 43.5
 Lewis, J., 25.36
 Light, J. R. C., 38.3

Linck, W., 41.1
 Lindholm, R. D., 33.1
 Lindner, E., 35.8
 Lindsay, J. K., 25.10
 Lippard, S. J., 18.3, 24.1
 Little, W. F., 22.7
 Lobach, M. I., 20.4
 Lorkowski, H. J., 25.11
 Love, J. L., 42.6
 Lupin, M. S., 38.2

M

McCleverty, J. A., 14.4, 43.3
 MacDiarmid, A. G., 10.3
 McDowell, M. V., 10.3
 Maddox, M. L., 37.2
 Magin, A., 28.19
 Mahler, J., 19.16
 Maitlis, P. M., 21.3
 Makarova, L. G., 1.15
 Makovetskii, K. L., 28.18
 Malatesta, L., 5.8, 31.8, 31.9, 43.6
 Mallan, J. M., 25.12
 Manakov, M. N., 31.10
 Mango, F. D., 35.9
 Manuel, T. A., 12.3
 Marchon, J. C., 42.12
 Markby, R., 28.26
 Martino, G., 42.13
 Mašek, J., 43.7
 Mason, R., 40.2, 40.5
 Massey, A. G., 16.6
 Mazzanti, G., 30.13
 Mehner, L., 41.1
 Mehrotra, R. C., 14.7
 Metzschker, H.-J., 41.1
 Miller, J. R., 4.29
 Mills, O. S., 40.6
 Milovskaya, E. B., 30.10
 Minami, S., 4.3
 Minkin, V. I., 39.2
 Misono, A., 28.14, 42.14
 Mitchell, P. C. H., 4.12
 Mittasch, A., 6.9
 Mizoroki, T., 28.15
 Moedritzer, K., 27.5
 Mond, R. L., 6.10, 6.11
 Moritani, I., 28.16
 Mortensen, L. E., 42.15
 Mrowca, J. J., 15.13

Muetterties, E. L., 11.10, 35.10
 Müller, E. W., 28.33
 Müller, H., 29.20
 Müller, O., 34.1
 Murray, R., 42.16
 Myers, R. R., 2.12

N

Nagy, P. L. I., 20.3
 Nakahara, M., 2.13
 Nakamura, A., 28.17
 Nast, R., 15.11
 Nasta, M. A., 10.3
 Natta, G., 30.11, 30.12, 30.13
 Nefedov, O. M., 31.10
 Nefedov, V. D., 3.3
 Nesmeyanov, A. N., 1.5, 25.13, 25.14,
 25.15, 25.16, 25.17, 25.18, 25.19
 Neubauer, D., 28.3
 Neumann, W. P., 1.6
 Neuse, E. W., 25.20, 25.21
 Nicholls, D., 4.9
 Nilsson, M., 2.14
 Nolan, M. J., 36.7
 Noltes, J. G., 4.36
 Nöth, H., 10.4
 Nottes, E. G., 2.15
 Nyholm, R. S., 11.9, 16.8, 19.10

O

Oberkirch, W., 20.6
 Ochiai, E., 29.21
 Ogata, I., 28.14
 Ogura, T., 22.10
 Ohm, H., 5.9
 Okhlobystin, O. Y., 1.7, 1.8, 1.15, 2.17,
 32.5
 Olivé, S., 30.8, 42.9
 Orchin, M., 19.11, 19.12, 29.22
 Osborn, J. A., 29.23
 Osipov, O. S., 39.2
 Otsuka, S., 2.16, 20.5, 31.11

P

Paiaro, G., 19.13
 Paris, A., 5.10
 Parshall, G. W., 15.12, 15.13
 Pasynkiewicz, S., 1.9
 Patat, F., 30.14, 30.15
 Pauson, P. L., 18.4, 18.5, 18.6, 25.22

Pavlov, O. N., 4.15
Pedotty, D. G., 35.6
Penfold, B., 11.11
Perevalova, E. G., 1.13, 25.17, 25.18, 25.19
Pettit, R., 19.14, 19.15, 19.16, 21.4, 21.5
Pietropaolo, R., 19.5
Pittman, C. U., 25.23
Plesske, K., 25.24
Podall, H., 5.11
Post, H. W., 4.6
Prinz, E., 30.4
Prokai, B., 15.10
Prokof'ev, A. K., 2.17, 32.5
Pruett, R. L., 22.2

Q

Quinn, H. W., 19.17

R

Ranganathan, S., 25.37
Rausch, M. D., 1.10, 16.9, 22.8, 25.25, 25.26, 25.27, 25.28, 25.29
Razuvaev, G. A., 4.4, 10.5, 10.7, 15.14, 15.15, 27.6
Reikhsfel'd, V. O., 28.18
Reimlinger, H., 29.17
Reis, H., 28.3
Reppe, W., 28.19
Rinehart, K. E., 25.3
Risen, W. M., 11.13
Robertson, G. B., 40.5
Rochow, E. G., 1.11, 1.12
Roper, W. R., 31.2
Rosca, S., 22.11
Rosenberg, H., 25.29
Rosenblum, M., 25.30
Rundell, C. A., 11.3
Rüttingen, R., 28.23
Ryang, M., 28.20

S

Saalfeld, F. E., 10.3
Sabel, A., 28.24
Saito, Y., 28.21
Sajus, L., 31.3, 42.13
Sasaki, Y., 11.12
Scharf, E., 29.20
Schlofer, H. L., 36.5

Schlögl, K., 25.31, 25.32, 25.33, 25.34
Schmid, G., 10.4, 10.6
Schmidbaur, H., 4.37
Schmidt, P. J., 19.11, 19.12
Schrauzer, G. N., 4.27, 14.5, 14.6, 28.22, 29.24, 34.4
Schunn, R. A., 35.10
Schwartz, W. T., 4.6
Schwarzhaus, K. E., 37.1
Schwochau, K., 4.16
Seibt, H., 29.20
Serée de Roch, I., 31.3
Sedlmeier, J., 28.23, 28.24
Setkina, V. N., 25.35
Shaw, B. L., 9.2, 19.2
Sheline, R. K., 12.1, 35.4
Shenkin, P., 25.36
Shihara, I., 4.5, 4.6
Shilov, A. E., 42.2
Shriver, D. F., 35.11
Shur, V. B., 42.19
Shvedov, V. P., 4.15
Sieber, R., 28.23
Sinn, H., 30.14, 30.15
Sinotova, E. N., 3.3
Skinner, H. A., 41.4
Sladkov, A. M., 15.16
Slocum, D. W., 25.36
Smidt, J., 28.23, 28.24
Smik, L., 5.7
Smith, D. C., 42.16
Sneeden, R. P. A., 4.10
Sokolik, R. A., 1.15
Sokolinskaya, T. A., 25.39
Sollich-Baumgartner, W. A., 29.13
Sonagashira, K., 3.4
Spacu, P. G., 6.12
Spasski, S. S., 4.7
Spengler, G., 4.13
Spiro, T. G., 36.6
Spitsyn, V. I., 1.13
Stafford, S. L., 37.2
Stalinski, B., 9.8
Steinrücke, E., 20.6
Stern, E. W., 28.25
Sternberg, H. W., 28.26
Stiddard, M. H. B., 8.2, 36.2
Stille, J. K., 30.16
Stolz, I. W., 12.1
Stone, F. G. A., 1.14, 2.18, 4.20, 5.2, 5.3, 7.1, 16.3, 16.10, 16.11

Stotskaya, L. L., 30.17

Strem, M., 5.12

Strohmeier, W., 27.7, 29.25, 33.3

Struchkov, Y. T., 11.2, 40.3

Stukan, R. A., 39.1

Sukhani, D., 14.7

Suvorov, A. L., 4.7

Swaminathan, S., 25.37

Szonyi, G., 29.26

T

Takegami, T., 15.17

Tanaka, K., 20.6, 28.4

Tatsumo, Y., 31.11

Taylor, K. A., 4.26

Teyssié, P., 30.7

Thayer, J. S., 4.34, 15.18

Tochtermann, W., 15.19

Todd, L. J., 26.4, 26.5

Tomkins, I. B., 9.9

Topchiev, A. V., 30.17

Toropova, M. A., 3.3

Tröber, A., 41.1, 41.2, 41.3

Trout, W. E., 6.13

Tsai, J. H., 19.17

Tsuji, J., 28.27, 28.28, 28.29

Tsutsui, M., 4.1, 15.20, 15.21, 22.12,
22.13, 28.30, 29.27

Tyfield, S. P., 8.1

U

Uchida, Y., 42.17

Ugi, I., 34.5

Ugo, R., 29.6, 29.28, 31.9, 31.12

Uguagliati, P., 19.5

Ukhin, L. Y., 15.16

V

Valot, H., 25.38

van der Kerk, G. J. M., 4.36

van Leeuwen, P. W. N. M., 37.3

van Meerssche, M., 40.7

van Tamelen, E. E., 42.18

Vaska, L., 31.13

Vishnyakova, T. P., 25.39

Vogel, M., 25.29

Volger, H. C., 37.3

Vol'kenau, N. A., 1.15

Vol'pin, M. E., 29.29, 42.19

von Kutepow, N., 28.3, 28.19, 28.31

Vrieze, K., 37.3

Vyazankin, N. S., 10.5, 10.7

W

Wada, K., 29.30

Wada, T., 16.12

Wagner, F., 34.1

Wagner, K., 41.1, 41.2, 41.3

Wailles, P. C., 4.2

Walter, D., 20.6

Waltz, W. L., 33.1

Wardlaw, N., 6.14

Wardlaw, W., 2.19

Watanabe, A., 4.8

Watters, K. L., 11.13

Watts, D. W., 33.1

Watts, L., 21.5

Watts, W. E., 25.40

Webster, D. E., 29.31

Welch, A. J. E., 6.15

Wells, P. B., 29.5, 29.31

Wender, I., 28.26

Werner, H., 2.20, 19.7, 20.2, 27.8

West, B. O., 13.3, 13.5

Whaley, T. P., 2.21

Wheatley, P. J., 40.8

White, D. A., 32.6

Wilke, G., 4.28, 20.6, 28.4, 28.12, 28.32,
28.33, 29.1

Wilkinson, G., 4.35, 22.3, 29.32, 31.14

Wittenberg, D., 29.20

Wright, C. M., 11.10

Wu, K.-L., 25.41

Y

Yamada, S., 25.42, 35.12, 40.9

Yamakawa, K., 25.1

Yamamoto, A., 29.33, 42.10

Yamazaki, H., 15.5, 18.1, 25.7

Yoshino, T., 31.15

Young, J. F., 10.8

Z

Zamoiskaya, L. V., 30.10

Zeiss, H. H., 4.10, 28.34

Zeitler, G., 5.5

Ziegler, K., 1.16, 28.35

Zimmer, W., 41.1

Zimmermann, H., 20.6

Zinato, E., 33.1

Subject Index

A

- Absolute integrated intensities of $\nu(\text{CO})$ bands, *see* Intensities of $\nu(\text{CO})$ bands
- Acetylene complexes
 - Group V metals, 56
 - substitution reactions, 352–355
 - cobalt, 354
 - platinum, 353
- Acrylonitrile complexes, 143, 144–146
- π -Allyl complexes, substitution reactions, 371–378
 - π,σ -rearrangements, 372
 - replacement of allyl groups, 373
 - π,π -transfer between metals, 374
- π -Allyl- π -cyclopentadienylpalladium, reactions, 388–389
- π -Allyliron complexes, 52
- π -Allylpalladium derivatives, 54, 373–378
 - reactions with $\text{Fe}_2(\text{CO})_9$, 374, 377
- Allyl halides, reactions with B_2Cl_4 , 259
- Aminoborylene complexes, 167
- Amino derivatives of metal carbonyls, 117
 - with bridging amino groups, 119
- π -Arene complexes, substitution, 365–370
- π -Arene- π -cyclopentadienyliron complexes, 44–47, 407
- NMR spectra, 85, 86
- Aromatic hydrocarbons, reactions with B_2Cl_4 , 260
- σ -Aryl complexes, 55, 56
- Associative mechanism of substitution in metal π -complexes, *see* Substitution
- Azaallene group, 163
- Azabutadiene complexes, 156
- Azides, reactions with metal carbonyls, 121, 129–131, 175, 184
- Azido complexes, 129, 184
- Azobenzene
 - complexes, 132, 133
 - reactions with Ni, Pd, and Pt compounds, 403–404

Azo compounds

- nitrogen-bridged iron carbonyl derivatives, 134
- ortho-metallated, 132
- reactions with metal carbonyls, 131–134

B

- Biological systems, organometallics in, 339
- 1,2-Bis(dichloroboryl)ethane
 - alkylation, 266
 - properties, 265–266
- Bonding, of carbonyl groups to metals, 208–211
- Borazoles, hexaalkyl, chromium complexes, 140
- Boron-boron bonds
 - bond energies, 248
 - formation by coupling reactions, 240
- Boronic acids, 243
- Boronium ions, 255
- Boron trihalides
 - reactions with sodium-potassium alloy, 240
 - synthesis of diboron tetrahalides from, 239
- Boroxoles, 243

C

- Camphenilone, organomercury derivatives, 23
- Carbamoyl complexes, 122
- Carbenes, amino, chromium complexes, 165
- Carbodiimides, reaction with $\text{Fe}(\text{CO})_5$, 163
- Catalysis by organometallics, 331–336
- β -Chlorovinyl ketones
 - complexes, 32
 - substitution reactions, 27
 - syntheses, 30–31
- Chlorovinyl-metal derivatives, 12, 13
- Chromium, substitution reactions of π -arene complexes, 366–370

- Chronopotentiometry of substituted ferrocenes, 100
- Cobalt, substitution of acetylene complexes, 354
- Cobalticinium salts, NMR spectra, 88
- Conjugation phenomena, 20
- Cotton-Kraihanzel method (CKM) intensity measurements, 218
- in metal carbonyl infrared spectra, 200, 213-214
- Cyanamides, dialkyl, metal complexes, 151
- Cyanate, metal carbonyl complexes, 173
- Cyano complexes of metal carbonyls, 168-173
- π -Cyclobutadiene palladium complexes, 390
- solvent effects on reactions, 381
- transfer of ligands, 378-383
- Cycloheptatriene, substitution in Group VI metal complexes, 364
- π -Cyclopentadienyl complexes
- π -arene iron derivatives, 44-47, 85, 86
- formation of ferrocene from, 383-384
- Group VII tricarbonyl complexes, 47-50
- ligand transfer reactions, 383, 390
- organotitanium derivatives, 50
- Cymantrene (π -cyclopentadienylmanganese tricarbonyl)
- NMR spectra, 89
- organic derivatives, 47-50
- as weak electron donor, 110
- D**
- Dialkylaminoboron derivatives
- coupling with sodium-potassium alloy, 240
- metathetical reactions, 242
- Diaryl mercury, by symmetrization reactions, 3
- Diazabutadiene complexes, 154
- Diazo compounds, reactions with metal carbonyls, 125-129
- Diazo-metal complexes, 125
- Diazonium organometallic syntheses, 4
- Diboration reactions, 251
- stereochemistry, 254
- Dichloroboryl derivatives
- from B_2Cl_4 , 251-254, 257, 258
- of ferrocene, 263
- reactions with hydrides, 267
- Diethyl azodicarboxylate, reactions with iridium compounds, 135
- Dinitrogen (N_2) complexes, reviews, 344
- Diphenyliodonium salts, 3
- Dissociation constants of ferrocenoic acids, 106
- E**
- Electron donor power
- of cymantrenyl group, 110
- of ferrocenyl group, 107
- σ values for metallocenyl groups, 109
- Electrophilic substitution reactions
- in ferrocenes, 39, 81
- orienting effect of ferrocenyl group, 40
- stereochemistry, 25
- Enolates
- metal derivatives, 17
- stereoisomerism, 17
- Ethyl diazoacetate, reaction with molybdenum complexes, 126
- Exchange reactions of organometallic compounds, 9
- isotopic exchange in ferrocenes, 80
- of ligands, 91
- F**
- Ferricinium salts, 407
- cyanation, 39
- Ferrocene
- electronic effects, 79-111
- electrophilic substitution, 81
- homoannular, 80
- isotopic exchange reactions, 80
- relative site reactivities, 80
- Ferrocene, dichloroboryl, 263
- Ferrocene derivatives
- chemistry developed by Russian School (Nesmeyanov), 37-44
- chronopotentiometry, 98, 100
- dissociation constants, 106
- infrared spectra, 104-106
- interannular electronic effects, 40, 101
- mass spectrometry, 95-97
- NMR spectra of heteroannularly substituted, 102-104
- oxidation-reduction potentials, 98
- primary substitution reactions, 39

Ferrocenes

formation

from other π -cyclopentadienyl complexes, 383, 384

of π -arene- π -cyclopentadienyliron salts, 407

ligand exchange, 44

stability of α -carbonium ions, 43

Ferrocenylammonium salts

anion exchange reactions, 43

photolysis, 42

Stevens rearrangement, 44

Ferrocenylboric acids, synthetic utility, 41

α -Ferrocenylcarbonium ions, stabilization, 107

Fulminate complexes, 178

G

Grignard reagents, 14

H

Halogenonium salts, 6

Heterocyclic compounds, π -bonded, 138

Hydrazine, reaction with rhenium compounds, 117

Hydrocarbon-metal π -complexes, 317-321

I

Infrared spectra

absolute integrated intensities, 222

heteroannularly substituted ferrocenes, 104

metal carbonyls, 199-233

solvent effects, 211-212

Intensities of $\nu(\text{CO})$ bands, 199-233

absolute, 222

hydrocarbon metal carbonyls, 227

iron carbonyl derivatives, 226, 228

$\text{M}(\text{CO})_5$ complexes, 225

metal carbonyls, 224

molybdenum carbonyl phosphine complexes, 229

nickel complexes, 228

polynuclear metal carbonyls, 230

measurement, 204-208

Bourgin's method, 207

direct integration, 205

Wilson-Wells method, 206

solvent effects, 211

Iron, π -arene- π -cyclopentadienyl cations, 44-47

Iron carbonyls

β -chlorovinyl ketone complexes, 32

structural data on nitrogen-bridged, 120

Isocyanates, reactions with metal carbonyls, 121

K

Ketenimine complexes, 158

L

Ligand exchange reactions

ferrocenes and arenes, 91

synproportionation, 93

Ligand substitution reactions in metal π -complexes, 347-409

acetylene complexes, 352-355

π -allyl complexes, 371-378

π -arene complexes, 365-370

π -cyclobutadiene derivatives, 378-383

π -cyclopentadienyl complexes, 383-409

mechanisms, 389

nature of transition state, 348

olefin complexes, 355-365

rearrangement of ligands, 351

Literature of organotransition metal

chemistry, *see* Organotransition metal chemistry

Local oscillating dipole method, 214

M

Manganese, organic derivatives of π -cyclopentadienyltricarbonyl complex, 47-50

Mass spectrometry

determination of B-B bond energies, 248

substituted ferrocenes, 95-97

Metal carbonyl cyanides, 168-173

Metal carbonyls

intensities of $\nu(\text{CO})$ bands in, 199-233

bond angles from, 216

nitrogen-donor complexes, 115-186

synthesis of $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$, 35

Metal π -complexes, *see* specific properties
 Metal-metal bonds, 310, 311
 syntheses, 36
 Metallocenes, 322, *see also* Ferrocene
 electronic effects, 79–111

N

Nickelocene, substitution reactions, 392–
 393, 401–406
 acetylenes, 405
 azobenzene, 403, 404
 iron carbonyl, 405
 Niobium, acetylene complexes, 56
 Nitrate derivatives, 182
 Nitrene complexes, 129, 136
 Nitric oxide, reaction with B_2Cl_4 , 263
 Nitriles
 π -bonded, 147
 metal carbonyl complexes, 141
 stability and bonding, 142–143
 syntheses, 148, 149
 Nitro (nitrito) derivatives, 183
 Nitrogen-bridged iron carbonyls, 119, 120
 Nitrogen (dinitrogen) complexes, 344
 Nitrogen donor complexes of metal car-
 bonyls, 115–186
 amino, 117
 aminoborylene, 167
 aminocarbene, 165
 azido, 129
 azo compounds, 131
 carbamoyl, 122
 dialkylcyanamide, 151
 diazo, 125
 heterocycles, π -bonded, 138–141
 ketenimine, 158
 methylenamine compounds, 160
 ortho-metallated, 157
 nitrene, 129
 nitriles, 141–151
 nitroso, 153
 phosphorimide, 164
 Schiff base complexes, 154
 o-semidine, 136
 ureylene, 121
 Norbornadiene complexes, solvolysis, 364
 Nuclear magnetic resonance spectroscopy
 π -arene- π -cyclopentadienyl iron cations,
 85

cobalticinium salts, 88
 cymantrenes, 89
 ferrocenes, 82
 chemical shifts, 83, 84
 heteroannularly substituted, 102
 titanocene derivatives, 104

O

Olefin complexes, substitution reactions,
 355–365
 platinum, 356
 rhodium, 360, 362
 Onium salts, syntheses, 6
 Organic syntheses via organometallics,
 327
 Organoboron compounds, thermal stabil-
 ity and disproportionation, 249
 Organodiboron derivatives containing
 boron–boron bonds, 237–269
 heterocyclic derivatives, 244–245
 preparation, 238–247
 thermochemical properties, 248
 Organoelement chemistry, 303
 Organo-Group IV compounds
 reactions with B_2X_4 , 261
 syntheses of organodiboranes, 247
 Organo-Group V compounds, 56
 Organomercury compounds, 10–12
 camphenilone derivative, 23
 stereochemistry of reactions, 27
 Organometallic compounds, syntheses via
 diazonium salts, 4
 Organometallic exchange reactions, 9,
 see also Ligand substitution reactions
 Organotitanium chemistry, 50
 Organotransition metal chemistry, 299–
 346
 biological systems, 339
 catalysis, 331–336
 π -complexes, 317–321
 electronic structures, 339
 fluorocarbon complexes, 315
 general, 300
 historical and biographical, 299
 Lewis base complexes, 312
 ligand reactivity, 337
 metal–carbon σ bonds, 313

- metal carbonyls, 306, 307, 309
 - anionic, 308
 - cationic, 309
- metal-metal bonds, 310, 311
- metallocarboranes, 325
- metallocenes, 322
- molecular nitrogen complexes, 344
- organic synthesis, 327
- organoelement chemistry, 303
- oxidative-addition reactions, 336
- photochemistry, 338
- physical methods, 340-342
- reaction kinetics and mechanisms, 326
- structural studies, 342
- techniques, 302
- Ortho-metallation
 - aromatic methyleneamines, 157
 - azo compounds, 132
- Oxidative addition reactions, 336
- Oxidation-reduction potentials of substituted ferrocenes, 98-101

P

- Phenylation reactions, 6
- Phosphorimide complexes, 164
- Platinum complexes, substitution reactions
 - acetylenes, 352-354
 - olefins, 356
- Pyrazolylborate complexes, 128

R

- π,σ -Rearrangements, 372
 - nickelocene, 401
- Redistribution reactions in organodiboron chemistry, 258
- Rhenium, π -cyclopentadienyl tricarbonyl derivatives, 47-50
- Ruthenocene, from ferrocene and RuCl_3 , 94
- Ruthenocenyl group, electron donor properties, 110

S

- Schiff base complexes, 154
 - ortho-metallated, 157
- Selenocyanate complexes, 180
- o*-Semidine derivatives, 136

- Stereochemistry
 - addition of B_2Cl_4 to multiple bonds, 254
 - σ,σ - and σ,π -conjugation, 23
 - electrophilic substitutions, 25
 - metal enolates, 17
- Structural data, nitrogen-bridged iron carbonyls, 120
- Substituent effects in metallocene chemistry, 79-111
 - ligand exchange, 91
 - metal-ring bond, 91
- Substitution
 - electrophilic, *see* Electrophilic substitution reactions
 - in metal π -complexes
 - associative mechanism of, 349, 370
 - of ligands, 347-409

T

- Tautomerism
 - metallotropic, 21
 - in organometallic compounds, 15
- Tetraalkoxydiborons, 249
- Tetrahalodiboranes(4), 242
 - addition to acetylenes and olefins, 251-253
 - alkylation, 246-247
 - aromatic hydrocarbons, 260
 - ferrocene, 263
 - haloolefins, 257-260
 - metathetical reactions, 242-247
 - organo-Group IV compounds, 241
 - thermal decomposition, 250
- Tetrakis (dialkylamino) diborons, reactions, 242
- Thiocyanate complexes, 177-180
- Titanium, π -cyclopentadienyl derivatives, 50, 384-388
- Transamination reactions of organoboron compounds, 244
- Transannular effects in ferrocenes, 40
- π,π -Transfer of ligands, 375
- Transition state in substitution reactions
 - of metal π -complexes, 348
 - five-coordinate, 349
 - importance of coordination number, 349, 351
- π -Trimethylenemethane complexes, 54

U

Ultraviolet spectra
cobalticinium salts, 91
ferrocenes, 90
Ureylene complexes, 121

V

Vinyl compounds
main group derivatives, 34

organometallic, 262
reactions with B_2Cl_4 and B_2F_4 , 257–
259
tin compounds, 261

Z

Zeise's salt, olefin substitution reactions,
361

Cumulative Subject Index: Volumes 6-10

Note: In general, for reference to organometallic compounds, *see* specific "organo-element" entries.

A

- Acetylenes
 - metal-catalyzed organic syntheses, **8**, 41-45
 - oxidative additions, **7**, 65-66
- Acrylonitrile complexes, **10**, 143-146
- Actinides, organic derivatives, **9**, 382-391
- Acylcobalt carbonyls, **6**, 123, 155
- Acylmetaloids, **7**, 98-139
- Acylsilanes, **7**, 100-102, 118-130
- π -Allyl complexes, **6**, 300-301; **7**, 195, 229-230; **8**, 29-83, 122-123, 277-283; **9**, 167, 386; **10**, 371-378
- σ -Allyl complexes, **7**, 178-195; **8**, 121
- Aluminum alkyls, **6**, 214-218; **8**, 179-183, 201-202
- Appearance potentials of organometallic ions, **6**, 315-323; **8**, 283-284, 315-319
- Aminoberyllium alkyls, **9**, 222-230
- Aminolead compounds, **7**, 289-296
- π -Arene-metal complexes, **6**, 290, 301; **7**, 196; **8**, 227-231; **9**, 171-172; **10**, 44-47, 365-370
- σ -Aryl complexes, **7**, 178-196; **9**, 171-172, 366; **10**, 55-56

B

- Benchrotrenes (benzene chromium tricarbonyls), **6**, 290, 306; **8**, 227-231, 289-290; **10**, 366-370
- Beryllium compounds, **6**, 203; **9**, 195-253
- Biological systems, transition metals in **7**, 203; **10**, 339
- Bis(cyclopentadienyl)titanium compounds, **9**, 162-170
- Bond dissociation energies, **8**, 284-286, 319-320
- Bonding, **8**, 100, 118
 - acylmetaloids, **7**, 131-139

- carbonyls, **10**, 208-211
 - electron deficient beryllium compounds, **9**, 197, 251-253
 - nitrosyls, **7**, 212
- Boranes, organic derivatives, **6**, 206-214; **8**, 199-200; **9**, 273, 300; **10**, 237-269
- Butadiene, oligomerization, **8**, 50-82
- Butadieneiron tricarbonyl derivatives, **6**, 306, 312; **8**, 265-269

C

- Carbene complexes, **7**, 197; **8**, 234; **9**, 421-424; **10**, 165
- Carbonium ions, metal complexes, **8**, 146-156
- Carbonylation reactions, **6**, 158-163; **7**, 198
- Carborane-metal complexes, **8**, 87-113
- Catalysis by organometallics
 - carbonylation, **6**, 158-163
 - hydroformylation, **6**, 128-136
 - olefin reactions, **7**, 199-202
 - organic syntheses by nickel compounds, **8**, 48-83
 - reviews, **10**, 331-336
- Cationic metal carbonyls, **8**, 117-159
- Chromium carbonyls, **8**, 133-159, *see also* Benchrotrenes
- Cobaloximes, **7**, 161, 203
- Cobalt carbonyl, **6**, 119-163; **8**, 152-155
- Cotton-Kraihanzel method, **10**, 213-214
- Coupling reactions, on nickel, **8**, 30-39, 82-83
- Cyclic hydrocarbons, syntheses, **8**, 48-74
- π -Cyclobutadiene-metal complexes, **6**, 285; **7**, 79; **8**, 99, 266; **10**, 378-383
- Cyclooctatetraene complexes, **8**, 233; **9**, 171, 385-390
- π -Cyclopentadienyl-metal carbonyls, **6**, 299-300; **8**, 124-137; **10**, 47-50
- nitrosyl carbonyls, **7**, 224-229

- π -Cyclopentadienyl-metal complexes, 6,
299-300; 8, 213-280; 9, 152-180,
367-391; 10, 44-47, 85-86, 383-384
Cyclosilanes, 7, 40
Cyclosilazanes, 9, 329-331, 337
Cymantrenes (cyclopentadienylmanganese
tricarbonyls), 6, 306, 310; 8, 235-
238; 10, 47-50, 110

D

- Decarbonylation by $(\text{Ph}_3\text{P})_3\text{RhCl}$, 7, 88-
89
Diazoalkanes, 7, 123; 9, 415-429; 10,
125-129
Dibenzene chromium, 6, 290
 π -Dicarbollyl complexes, 8, 91-100
 π -Dienyliron cations, 8, 146-150
 β -Diketone complexes, 9, 150-151
Dinitrogen (N_2) complexes, 7, 65-67, 166,
203; 9, 185-188; 10, 344
Dipole moments, 7, 173-174
Disproportionation reactions, 6, 32

E

- Electrochemical syntheses of organometal-
lics, 6, 15; 7, 246; 8, 129
Electronic spectra
alkyls and aryls, 7, 171-172
allyl complexes, 8, 108-109
nitrosyls, 7, 233
organo-Group IV compounds, 7, 41-
43, 114, 147
Electron spin resonance spectra
alkyls and aryls, 7, 173
anion radicals from acylsilanes, 7, 138
metal nitrosyls, 7, 234
phosphine methylenes, 9, 298
Elimination reactions, 7, 166-167
Exchange reactions
ferrocenes, 10, 80, 91
organo-Group II compounds, 8, 170-
176
organo-Group III compounds, 8, 179-
183, 187-203
organo-Group IV compounds, 7, 271
organolithium compounds, 8, 168-170
organometallics, 8, 167-205; 9, 9, 375

F

- Ferrocenes
mass spectra, 6, 285-286, 308-310; 8,
241-257
polysilane derivatives, 6, 70-77, 96-108
reactions, 10, 37-44, 383-384, 407
substituent effects, 10, 79-111
Ferrocenophanes, 6, 305; 8, 254-255
Fluorocarbon complexes, 6, 292, 302; 8,
270-281
Free radicals, 7, 28

G

- Germanium compounds, 6, 236-242; 9,
308-309
Grignard reagents, 6, 205; 7, 1-7; 8, 171-
173; 9, 365, 428
Group IV keto derivatives, 7, 96-153

H

- Heterocycles, inorganic, 9, 329-348
 α -Heterodiazoalkanes, 9, 397-429
Homogeneous catalysis and oxidative ad-
dition reactions, 7, 84-90
Hydrocarbon-metal π complexes, 10,
317-321
Hydroformylation reaction, 6, 124-128,
138-145; 7, 87-88
Hydrogenation reactions, 6, 147-151; 7,
84-87
Hydrogen transfer, 8, 75-80, 126-127
Hydroplumbation, 7, 279-289
Hydrosilation, 6, 151

I

- Indenyl complexes, 8, 263-264; 9, 376-
378
Infrared spectra
acyl-Group IV compounds, 7, 107, 147
alkyls and aryls, 7, 170-171
metal carbonyls, 10, 199-233
metal nitrosyls, 7, 231-232
Inorganic ring systems, 9, 329-348
Insertion reactions, 6, 129
allyl-nickel complexes, 8, 40-48
carbenes, 9, 415-424
metal alkyls and aryls, 7, 189-195

Intensities of $\nu(\text{CO})$ bands, **10**, 199-233
Iridium complexes, **7**, 63-65, 84; **8**, 155-157

Iron carbonyl complexes

diaryldiazomethanes, **9**, 429; **10**, 125-129

halides, **8**, 13-14

mass spectra, **6**, 275-279; **8**, 259-271

nitrogen-bridged, **10**, 120

nitrosyls, **8**, 10-11, 21-22, 145

Isomerization reactions, **6**, 153-155

K

β -Keto-Group IV compounds, **7**, 143-152

Ketones, synthesis via organometallics, **6**, 135-136, 144

L

Lanthanides, **9**, 361-380

Lead compounds, **6**, 247-250; **7**, 245-256

Ligand substitution reactions in metal π -complexes, **10**, 347-409

Lithium alkyls, **6**, 202; **8**, 168-170

M

Mass spectra of organometallic complexes, **6**, 273-323; **8**, 211-327

appearance potentials, **6**, 315-323; **10**, 248

σ -bonded complexes, **6**, 285, 293, 302; **7**, 172

carbonyls, **6**, 275, 298-299

cyclosilanes, **7**, 34

dialkylberylliums, **9**, 199

ferrocenes, **6**, 304, 308; **8**, 241-259; **10**, 95-97

hydrocarbon π -complexes, **6**, 284-295, 300-302; **8**, 211-327

nitrosyls, **6**, 282, 298; **7**, 234

Mercury compounds, **6**, 256-260

Metal carbonyls, **8**, 1-24

infrared spectra, **10**, 199-233

mass spectra, **6**, 278-280, 298-299

Metal nitrosyls, **6**, 282

Metallation reactions, **7**, 15-19

Metallocenes

mass spectra, **8**, 211-327

substituent effects, **10**, 79-111

Mössbauer spectra, **7**, 234

organotin compounds, **9**, 21-134

N

Nickel in organic syntheses, **6**, 14; **8**, 29-83, 278-283

Nickelocene, substitution reactions, **10**, 392-393, 401-406

Nitrile complexes, **10**, 141-149

Nitrogen complexes, *see* Dinitrogen complexes

Nitrogen-donor complexes of metal carbonyls, **10**, 115-186

Nitrosyl complexes, **7**, 211-236

Nitrosyl metal carbonyls, **7**, 216-222; **8**, 21-22, 223

Nuclear magnetic resonance spectroscopy alkyls and aryls, **7**, 168-170

fast exchange reactions, **8**, 167-205

metallocenes, **10**, 85-89, 102-104

nitrosyls, **7**, 234

organoberyllium compounds, **9**, 217-219, 246

organo-Group III derivatives, **8**, 193-196

organo-Group IV derivatives, **7**, 117, 149; **9**, 12-15, 58

organopolysilanes, **6**, 85-88

phosphine methylenes, **9**, 293-295, 297

redistribution equilibria studies, **6**, 186-193

stereochemistry of phosphine complexes, **7**, 59-60

O

Olefin complexes, **6**, 301-302; **7**, 197; **8**, 264-271, 276-277; **10**, 355-365

Olefins

dimerization, **7**, 89, 199

isomerization, **6**, 124-128

polymerization, **6**, 12; **9**, 182-185

π -Ollyl complexes, **8**, 87-113

Organoactinides, **9**, 382-391

Organoaluminum compounds, **7**, 270; **8**, 179-187, 193-198, 201-202; **9**, 344-347

Organoberyllium compounds, **7**, 11; **8**, 170-171; **9**, 195-253

Organoboron compounds, **10**, 237-269

Organocadmium compounds, **8**, 174-175;
 9, 286-288
Organogallium compounds, **8**, 187-190;
 9, 344-346
Organolanthanides, **9**, 365-382
Organolead compounds, **7**, 242-303
Organolithium compounds, **7**, 7-11; **8**,
 168-170, 177-179
Organometallic exchange reactions, **7**,
 15-21
Organometallic nitrosyl complexes, **7**,
 211-236
Organophosphine derivatives, **9**, 278-290
Organopolysilanes, **6**, 19-110
Organosilicon compounds, **6**, 19-110; **7**,
 38; **9**, 302-308
Organothallium compounds, **7**, 23-25
Organotin compounds, Mössbauer
 studies, **9**, 21-134
Organotitanium compounds, **9**, 135-188;
 10, 384-388
Organotransition metal chemistry, **10**,
 273-346
Osmium complexes, **7**, 72-74; **8**, 143-144
Oxidative addition reactions of transition
 metal complexes, **7**, 54-90, 162-164;
 8, 107; **10**, 336
Oxo reaction, *see* Hydroformylation re-
 action

P

Phosphine complexes, **6**, 294-296, 302-
 303; **8**, 5, **8**, 14
Phosphorus compounds, **9**, 278-290
Physical methods in organotransition
 metal chemistry, **10**, 340-342
Platinum metal carbonyls, **8**, 14-17, 158-
 159
Polymerization of olefins, **6**, 12; **9**, 182-
 185
Polysilanes, **6**, 65-80

R

Reaction mechanisms, **6**, 193; **7**, 84, 235,
 279
 π,σ -Rearrangements, **10**, 372
Redistribution reactions, **6**, 171-262; **7**,
 247; **9**, 324; **10**, 258
Rhodium complexes, **6**, 67, 89-90; **8**,
 155-156, 276-277

S

Schiff-base complexes, **6**, 295; **10**, 154,
 157
Silicon compounds, **6**, 41-45, 65-80; **9**,
 269-273, 308-314
Siloxanes, **6**, 39-40
Spectroscopy, *see* Electronic, Electron
 spin resonance, Infrared, Mössbauer,
 Nuclear magnetic resonance spectra
Stereochemistry of reactions, **7**, 59-60,
 123-128; **10**, 23, 25, 254

T

Thorium complexes, **9**, 386-388
Tin compounds, **6**, 243-247; **9**, 21-134
Titanium complexes, **9**, 135-188; **10**,
 384-388
Transition metal complexes, organo-
 metallic
 alkyls and aryls, **7**, 157-204
 carborane complexes, **8**, 87-113
 ligand substitution reactions, **10**, 347-
 409
 mass spectra, **6**, 273-323; **8**, 211-327
 oxidative-addition reactions, **7**, 54-90,
 162-164
 redistribution reactions, **6**, 256-262
 reviews, **10**, 299-346
Transuranium elements, **9**, 389-391

U

Uranium compounds, **9**, 382-386

V

Vanadium complexes, **8**, 131-133, 216-
 218
Vaska's compound, **7**, 59-61, 70-79; **9**,
 422
Vinylsilanes, **6**, 79

W

Wilkinson's complex, **7**, 69, 85-88

Z

Ziegler catalysts, **6**, 11-12; **9**, 182-185
Zirconium complexes, **6**, 287; **8**, 214-215

Cumulative List of Contributors

- Abel, E. W., **5**, 1; **8**, 117
 Aguiló, A., **5**, 321
 Armitage, D. A., **5**, 1
 Atwell, W. H., **4**, 1
 Bennett, M. A., **4**, 353
 Birmingham, J., **2**, 365
 Brook, A. G., **7**, 95
 Brown, T. L., **3**, 365
 Bruce, M. I., **6**, 273; **10**, 273
 Cais, M., **8**, 211
 Cartledge, F. K., **4**, 1
 Chalk, A. J., **6**, 119
 Churchill, M. R., **5**, 93
 Coates, G. E., **9**, 195
 Collman, J. P., **7**, 53
 Coutts, R. S. P., **9**, 135
 Coyle, T. D., **10**, 237
 Cullen, W. R., **4**, 145
 de Boer, E., **2**, 115
 Dessy, R. E., **4**, 267
 Emerson, G. F., **1**, 1
 Ernst, C. R., **10**, 79
 Fritz, H. P., **1**, 239
 Fuson, R. C., **1**, 221
 Gilman, H., **1**, 89; **4**, 1; **7**, 1
 Green, M. L. H., **2**, 325
 Griffith, W. P., **7**, 211
 Gubin, S. P., **10**, 347
 Gysling, H., **9**, 361
 Harrod, J. F., **6**, 119
 Heck, R. F., **4**, 243
 Heimbach, P., **8**, 29
 Hieber, W., **8**, 1
 Jolly, P. W., **8**, 29
 Kaesz, H. D., **3**, 1
 Kettle, S. F. A., **10**, 199
 Kilner, M., **10**, 115
 King, R. B., **2**, 157
 Kitching, W., **4**, 267
 Köster, R., **2**, 257
 Kühlein, K., **7**, 241
 Kuivila, H. G., **1**, 47
 Kumada, M., **6**, 19
 Lappert, M. F., **5**, 225; **9**, 397
 Luijten, J. G. A., **3**, 397
 Lupin, M. S., **8**, 211
 Maddox, M. L., **3**, 1
 Maitlis, P. M., **4**, 95
 Manuel, T. A., **3**, 181
 Mason, R., **5**, 93
 Moedritzer, K., **6**, 171
 Morgan, G. L., **9**, 195
 Mrowca, J. J., **7**, 157
 Nagy, P. L. I., **2**, 325
 Nesmeyanov, A. N., **10**, 1
 Neumann, W. P., **7**, 241
 Okawara, R., **5**, 137
 Oliver, J. P., **8**, 167
 Onak, T., **3**, 263
 Parshall, G. W., **7**, 157
 Paul, I., **10**, 199
 Pettit, R., **1**, 1
 Poland, J. S., **9**, 397
 Prokai, B., **5**, 225
 Rijkens, F., **3**, 397
 Ritter, J. J., **10**, 237
 Rochow, E. G., **9**, 1
 Roper, W. R., **7**, 53
 Rubezhov, A. Z., **10**, 347
 Schmidbaur, H., **9**, 259
 Schrauzer, G. N., **2**, 1
 Schwebke, G. L., **1**, 89
 Skinner, H. A., **2**, 49
 Slocum, D. W., **10**, 79
 Stafford, S. L., **3**, 1
 Stone, F. G. A., **1**, 143
 Tamao, K., **6**, 19
 Thayer, J. S., **5**, 169
 Todd, L. J., **8**, 87
 Treichel, P. M., **1**, 143
 Tsutsui, M., **9**, 361
 Tyfield, S. P., **8**, 117
 van der Kerk, G. J. M., **3**, 397
 Wada, M., **5**, 137
 Wailes, P. C., **9**, 135
 West, R., **5**, 169
 Wilke, G., **8**, 29
 Ziegler, K., **6**, 1
 Zuckerman, J. J., **9**, 21

Cumulative List of Titles

- Alkali Metal Derivatives of Metal Carbonyls, **2**, 157
Alkyl and Aryl Derivatives of Transition Metals, **7**, 157
Alkylcobalt and Acylcobalt Tetracarbonyls, **4**, 243
Allyl Metal Complexes, **2**, 325
 π -Allylnickel Intermediates in Organic Synthesis, **8**, 29
Applications of ^{119}mSn Mössbauer Spectroscopy to the Study of Organotin Compounds, **9**, 21
Carboranes and Organoboranes, **3**, 263
Catalyses by Cobalt Carbonyls, **6**, 119
Catenated Organic Compounds of the Group IV Elements, **4**, 1
Conjugate Addition of Grignard Reagents to Aromatic Systems, **1**, 221
Cyclobutadiene Metal Complexes, **4**, 95
Cyclopentadienyl Metal Compounds, **2**, 365
Diene-Iron Carbonyl Complexes, **1**, 1
Electronic Effects in Metallocenes and Certain Related Systems, **10**, 79
Electronic Structure of Alkali Metal Adducts of Aromatic Hydrocarbons, **2**, 115
Fast Exchange Reactions of Group I, II, and III Organometallic Compounds, **8**, 167
Fluorocarbon Derivatives of Metals, **1**, 143
Heterocyclic Organoboranes, **2**, 257
 α -Heterodiazoalkanes and the Reactions of Diazoalkanes with Derivatives of Metals and Metalloids, **9**, 397
Infrared Intensities of Metal Carbonyl Stretching Vibrations, **10**, 199
Infrared and Raman Studies of π -Complexes, **1**, 239
Insertion Reactions of Compounds of Metals and Metalloids, **5**, 225
Isoelectronic Species in the Organophosphorus, Organosilicon, and Organoaluminum Series, **9**, 259
Keto Derivatives of Group IV Organometalloids, **7**, 95
Lewis Base-Metal Carbonyl Complexes, **3**, 181
Ligand Substitution in Transition Metal π -Complexes, **10**, 347
Mass Spectra of Metallocenes and Related Compounds, **8**, 211
Mass Spectra of Organometallic Compounds, **6**, 273
Metal Carbonyl Cations, **8**, 117
Metal Carbonyls, Forty Years of Research, **8**, 1
Metal π -Complexes Formed by Seven- and Eight-Membered Carbocyclic Compounds, **4**, 353
Nitrogen Groups in Metal Carbonyl and Related Complexes, **10**, 115
Nitrosyls, **7**, 211
Nuclear Magnetic Resonance Spectra of Organometallic Compounds, **3**, 1
Of Time and Carbon-Metal Bonds, **9**, 1
Olefin Oxidation with Palladium Catalyst, **5**, 321
Organic Chemistry of Lead, **7**, 241
Organic Complexes of Lower-Valent Titanium, **9**, 135
Organic Substituted Cyclosilanes, **1**, 89
Organoarsenic Chemistry, **4**, 145
Organoberyllium Compounds, **9**, 195

- Organolanthanides and Organoactinides, **9**, 361
Organometallic Aspects of Diboron Chemistry, **10**, 237
Organometallic Chemistry, A Forty Years' Stroll, **6**, 1
Organometallic Chemistry, My Way, **10**, 1
Organometallic Chemistry of Nickel, **2**, 1
Organometallic Chemistry, Some Personal Notes, **7**, 1
Organometallic Nitrogen Compounds of Germanium, Tin, and Lead, **3**, 397
Organometallic Pseudohalides, **5**, 169
Organometallic Reaction Mechanisms, **4**, 267
Organopolysilanes, **6**, 19
Organosulphur Compounds of Silicon, Germanium, Tin, and Lead, **5**, 1
Organotin Hydrides, Reactions with Organic Compounds, **1**, 47
Organo-Transition Metal Chemistry—A Guide to the Literature 1950–1970, **10**, 273
Oxidative-Addition Reactions of d^8 Complexes, **7**, 53
Redistribution Equilibria of Organometallic Compounds, **6**, 171
Strengths of Metal-to-Carbon Bonds, **2**, 49
Structural Aspects of Organotin Chemistry, **5**, 137
Structural Chemistry of Organo-Transition Metal Complexes, **5**, 93
Structures of Organolithium Compounds, **3**, 365
Transition Metal-Carborane Complexes, **8**, 87

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